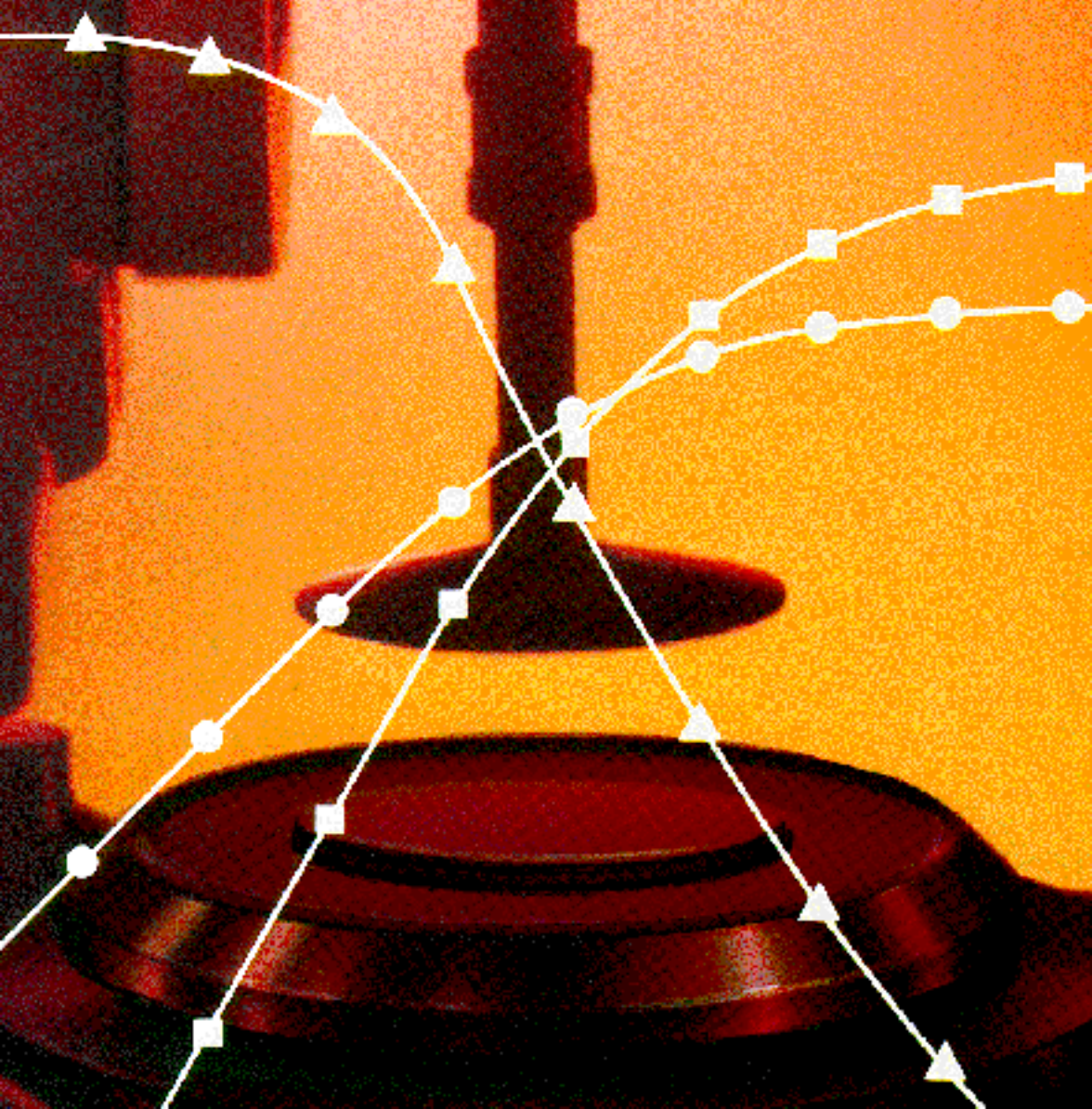


A Practical Approach to Rheology and Rheometry

by
Gebhard Schramm



**A Practical Approach to
Rheology and Rheometry**

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2nd Edition

Gebrueder HAAKE GmbH, Karlsruhe,
Federal Republic of Germany

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Preface

Some 15 years ago HAAKE published a booklet "Introduction to Practical Viscometry" which was translated into 7 languages and thus reached many readers worldwide. In the Seventies it was our intention to lecture on viscometry in as many countries as possible to make people aware of what non-Newtonian flow behavior meant and what the technical consequence of the shear rate dependency of many technically important fluids is. At that time in many technical branches such as in the paint industry, the "Ford-cup" was still considered a sufficient tool for foremen in factories to classify paint batches as "good" or "bad". Orifice viscometers available under the names of Redwood, Sayboldt etc. were priced at some \$100 a piece. Rotational viscometers with a rotor speed programmer and a suitable x/t-recorder were sold at prices almost 100 times higher. It must have caused some amusement at management level when laboratories asked for such large amounts of money for a new rotational viscometer while the "cups" were cheap, unbreakable and had been sufficient for quality control for such a long time. HAAKE is proud for having contributed with its' rotational viscometers, worldwide seminars on viscometry and the above mentioned booklet to the understanding of viscometry as a small but important segment of physics. The growing interest in viscometry during the last decades has led to an astonishing increase in the numbers of viscometers sold, which in turn have found users worldwide both in scientific research and in industrial applications.

The HAAKE management in the Seventies, of course, knew of the work of the famous Prof. Weissenberg, who already proved that most fluids in their response to shear stresses exhibited both viscous flow and elastic deformation as soon as the early Forties. Prof. Weissenberg also developed the "Rheogoniometer", which for the first time enabled the measurement of both the corresponding shear stress signal defining viscosity and the normal force signal characterizing elasticity at a given shear rate. This first top-class rheometer was (by today's standards) bulky and heavy and it was priced at a quarter of a million dollars, which limited its sale to only a few outstanding research laboratories around the world. It has been said that in some 30 years only a few hundred of these instruments were actually made and this may have contributed to the fact that the manufacturer eventually dropped this product line. We at HAAKE in 1970 did not dare to offer such highly sophisticated rheometers, which were indeed better than Ford-cups but were priced some 2000-times higher.

The last 15 years have seen great changes in the field of rheology and rheometry:

Universities and technical colleges are now offering courses in rheometry and its usage in scientific and technical applications in increasing numbers. Thou-

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sands of physicists, chemists and engineers have now understood that in rheology, viscosity and elasticity are linked to each other as closely as “men and women in the human race”: one should not regard one as more important than the other and certainly not completely ignore one factor in favour of the other!

Machine tools have improved so much that for instance air bearings with machining tolerances of microns can be regarded as “normal” and strain sensors have been developed that divide a 360° revolution into 1000000 increments or even more. This has led to modern rheometers with a measuring sensitivity which allows an insight into rheological responses which people two decades ago could only have dreamt of.

All this would still not have led to much if computerization had not become “everybody’s tool” within the last ten years with computer prices dropping unbelievably and their capabilities increasing at the same time. We cannot promote dynamic tests in quality control departments unless a computer can handle phase shifts of sinusoidal waves of strain inputs and resulting stress responses by means of a Fourier analysis. Equally, only computers can evaluate “creep and recovery tests” with regression calculations to differentiate between elasticity and viscosity responses as a function of shear history and recovery time. Data evaluation is carried out automatically in a minute or two by people whose mathematical training does not go much beyond simple calculus.

15 years have passed since the first edition of “Introduction to Practical Viscometry” appeared and it is time for a fully revised version including chapters which had then been omitted intentionally and those about which we could not have reported because test methods were not yet fully developed. There are very many good books and papers by famous rheologists such as Walters, Ferry, Cheng, Laun, Gleissle etc. which scientifically-minded readers should refer to. Their works are often quite large volumes which are sometimes difficult to read and comprehend for beginners to rheology. It is hoped that this book, in trying to give simple explanations for often complex phenomena and giving advice on “what to do and what not to do”, can induce readers to gain an insight into a field that is scientifically and technically fascinating and commercially rewarding.

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1. Introduction to Rheometry

Rheology describes the deformation of a body under the influence of stresses. “Bodies” in this context can be either solids, liquids, or gases.

Ideal solids deform elastically. The energy required for the deformation is fully recovered when the stresses are removed.

Ideal fluids such as liquids and gases deform irreversibly – they flow. The energy required for the deformation is dissipated within the fluid in the form of heat and cannot be recovered simply by removing the stresses.

The real bodies we encounter are neither ideal solids nor ideal fluids.

Real solids can also deform irreversibly under the influence of forces of sufficient magnitude – they creep, they flow.

Example: Steel – a typical solid – can be forced to flow as in the case of sheet steel when it is pressed into a form, for example for automobile bodyparts.

Only a few liquids of technical or practical importance come close to ideal liquids in their behavior. The vast majority of liquids show a rheological behavior that classifies them to a region somewhere between the liquids and the solids: they are in varying extents both elastic and viscous and may therefore be named “visco-elastic”. Solids can be subjected to both tensile and shear stresses while such as water can only be sheared.

This classification of the rheological behavior of materials related to their response to applied stresses must be further extended by the introduction of the time-scale of any deformation process:

It is written in the bible that “everything flows, if you wait long enough, even mountains ...”

For all materials a characteristic time factor “ λ ” can be determined which is infinite in size for ideal elastic solids and almost zero for liquids such as water ($\lambda_w = 10^{-12}$ s). On the other hand deformation processes relate to characteristic time values “ t ”. A high “Deborah number” (λ/t) defines a solid-like behavior and a low “Deborah number” defines a liquid-like behavior.

Two examples may help to improve the understanding of the above:

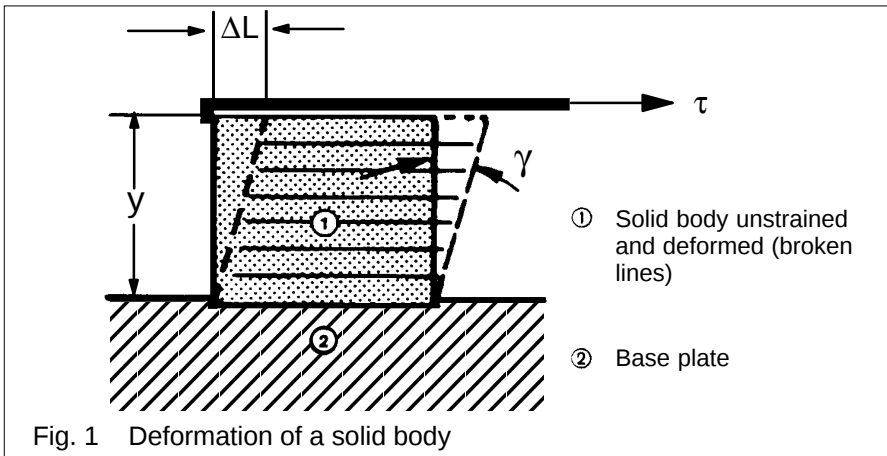
- a) If water is ejected from a nozzle at a very high speed and the droplets hit a hard wall, they will flatten. The droplets then spring back and recover their sphere shape in “no time” as the result of elasticity and surface tension. At these extremely fast deformation processes – “ t ” being very small results in the Deborah-number being high – even water with its low λ -value reacts elastically.

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- b) The famous glass windows of the Cathedral of Chartres in France have “flowed” since they were produced some 600 years ago. The glass panes had a uniform thickness from top to bottom in mediaeval times, but today the glass molecules have flown under the influence of gravity so that the thickness at the top is now “paper-thin” while the pane thickness has more than doubled at the bottom. The very long time t of this flow process results in a small Deborah-number. Thus one can state that solid glass, in spite of its high λ -value at room temperature under conditions as stated above, belongs to the group of fluids ... if you wait long enough!
- An important conclusion of the concept of Deborah numbers is: substances such as water or glass cannot be classed as liquids or solids as such, but rather they exhibit a liquid or solid behavior under certain conditions of stress, shear rates or time.

Ideal solids subjected to shear stresses react with strain:



$$\tau = G \cdot \frac{dL}{dy} = G \cdot \tan \gamma \approx G \cdot \gamma \quad [1]$$

$$\tau = \text{shear stress} = \text{force} / \text{area} \left[\frac{N}{m^2} = Pa \right]$$

$$G = \text{Young's modulus that relates to the stiffness of the solid} \left[\frac{N}{m^2} \right]$$

$$\gamma = \frac{dL}{y} = \text{strain (dimensionless)}$$

y = height of the solid body [m]

ΔL = deformation of the body as a result of shear stress [m].

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The Young's modulus G in this equation is a correlating factor indicating stiffness linked mainly to the chemical-physical nature of the solid involved. It defines the resistance of the solid against deformation.

The resistance of a fluid against any irreversible positional change of its' volume elements is called viscosity. To maintain flow in a fluid, energy must be added continuously.

While solids and fluids react very differently when deformed by stresses there is no basic difference rheologically between liquids and gases; gases are just fluids with a much lower viscosity, for example hydrogen gas at 20°C has a viscosity a hundredth of the viscosity of water.

A difference between a liquid and a gas worth noting is that their viscosities are inversely dependent on temperature.

Instruments which measure the visco-elastic properties of solids, semi-solids and fluids are named "rheometers". Instruments which are limited in their use for the measurement of the viscous flow behavior of fluids are described as "viscometers".

In this book dealing with rheometers/viscometers and their usage for solids and liquids, the measurement of the viscosity of gases will not be dealt with.

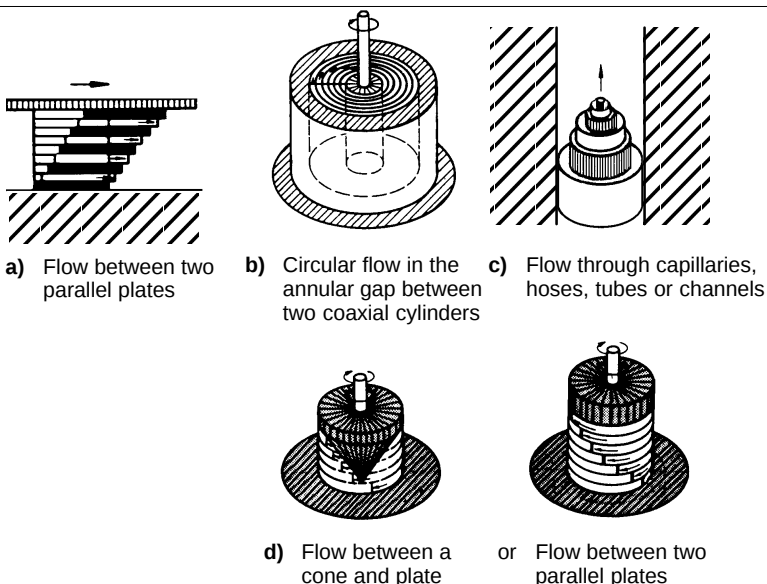


Fig. 2 Various types of flow models

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Shear induced flow in liquids can occur in 4 laminar flow model cases:

a) **Flow between two parallel flat plates,**

when one plate moves and the other is stationary. This creates a laminar flow of layers which resembles the displacement of individual cards in a deck of cards. Conditions remain similar when the upper plate is acting as a stationary doctor blade used in a coating process on flat boards. The coating material – paint or glue – is subjected to a laminar flow in the small gap that is formed between the board and the blade.

b) **Flow in the annular gap between two concentric cylinders.**

One of the two is assumed to be stationary while the other can rotate. This flow can be understood as the displacement of concentric layers situated inside of each other. A flow of this type is realized for example in sleeve bearings and in rotational rheometers with coaxial cylinder sensor systems.

c) **Flow through pipes, tubes, or capillaries.**

A pressure difference between the inlet and the outlet of a capillary forces a Newtonian liquid – the term will be explained in the following – to flow with a parabolic speed distribution across the diameter. This resembles a telescopic displacement of nesting, tube-like liquid layers sliding over each other. A variation of capillary flow is the flow in channels with a rectangular cross-section such as slit capillaries. If those are used for capillary rheometry the channel width should be wide in comparison to the channel depth to minimize the side wall effects.

d) **Flow between two parallel-plate- or between cone-and-plate sensor systems of rotational rheometers**

when one of the two is stationary and the other rotates. This model resembles twisting a roll of coins causing coins to be displaced by a small angle with respect to adjacent coins. This type of flow is caused in rotational rheometers with the samples placed within the gap of parallel-plate or cone-and-plate sensor systems.

2. Aspects of Rheometry

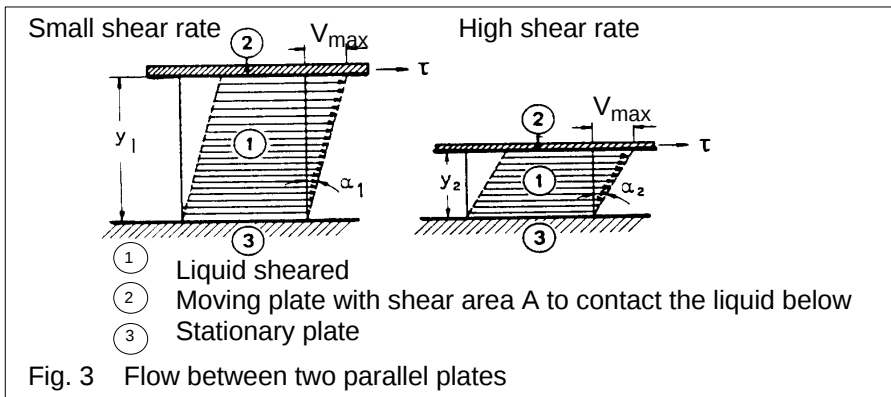
2.1 The basic law

The measurement of the viscosity of liquids first requires the definition of the parameters which are involved in flow. Then one has to find suitable test conditions which allow the measurement of flow properties objectively and reproducibly. Isaac Newton was the first to express the basic law of viscometry describing the flow behaviour of an ideal liquid:

$$\tau = \eta \cdot \dot{\gamma} \quad [2]$$

shear stress = viscosity · shear rate

The parallel-plate model helps to define both shear stress and shear rate:



2.2 Shear stress

A force F applied tangentially to an area A being the interface between the upper plate and the liquid underneath, leads to a flow in the liquid layer. The velocity of flow that can be maintained for a given force is controlled by the internal resistance of the liquid, i.e. by its viscosity.

$$\tau = \frac{F_{(force)}}{A_{(area)}} = \frac{N_{(Newton)}}{m^2} = Pa [Pascal] \quad [3]$$

The unit “Pascal” has replaced the former unit “dyne/cm²” which was previously used for stresses especially in scientific literature.

$$1 Pa = 10 \text{ dyne/cm}^2$$

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2.3 Shear rate

The shear stress τ causes the liquid to flow in a special pattern. A maximum flow speed $v_{\max}$ is found at the upper boundary.

The speed drops across the gap size y down to $v_{\min} = 0$ at the lower boundary contacting the stationary plate. Laminar flow means that infinitesimally thin liquid layers slide on top of each other, similar to the cards in a deck of cards. One laminar layer is then displaced with respect to the adjacent ones by a fraction of the total displacement encountered in the liquid between both plates. The speed drop across the gap size is named “shear rate” and in it’s general form it is mathematically defined by a differential.

Please note

Inasmuch as normal typewriters and computers are not able to print “ $\dot{\gamma}$ ” it is also common to use the letter “D” to indicate shear rate.

$$\dot{\gamma} = \frac{dv}{dy} \quad [4]$$

$$\dot{\gamma} = \frac{m/s}{m} = \frac{1}{s} = [s^{-1}]$$

In case of the two parallel plates with a linear speed drop across the gap the differential in the equation reduces to:

$$\dot{\gamma}_{\max} = \frac{v_{\max}}{y} [s^{-1}] \quad [5]$$

Please note

In the scientific literature shear rate is denoted as $\dot{\gamma}$. The dot above the γ indicates that shear rate is the time-derivative of the strain caused by the shear stress acting on the liquid lamina.

$$\dot{\gamma} = \frac{d\gamma}{dt} = \frac{dL}{dy} = \frac{dv}{dy} \quad [6]$$

Equation [2] can be expanded:

$$\tau = \eta \cdot \frac{dv}{dy} = \eta \cdot \dot{\gamma} \quad [7]$$

Comparing equations [1] and [7] indicates another basic difference between solids and liquids: Shear stress causes strain in solids but in liquids it causes the rate of strain. This simply means that solids are elastically deformed while liquids flow. The parameters G and η serve the same purpose of introducing a resistance factor linked mainly to the nature of the body stressed.

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2.4 Dynamic viscosity

Solving equation [2] for the dynamic viscosity η gives:

$$\eta = \frac{\tau}{\dot{\gamma}} \quad [8]$$

$$\eta = \frac{N}{m^2} \cdot s = Pa \cdot s$$

The unit of dynamic viscosity η is the “Pascal · second” [Pa·s]. The unit “milli-Pascal · second” [mPa·s] is also often used.

$$1 Pa \cdot s = 1000 mPa \cdot s$$

It is worthwhile noting that the previously used units of “centiPoise” [cP] for the dynamic viscosity η are interchangeable with [mPa·s].

$$1 mPa \cdot s = 1 cP$$

Typical viscosity values at 20°C [mPa·s] :

Petrol	0.65	Coffee cream	≈ 10
Water	1.0	Honey	≈ 10 ⁴
Mercury	1.5	Polymer melts	≈ 10 ³ – 10 ⁶
Grape juice	2 - 5	Bitumen	≈ 10 ⁸
Blood [at 37°C]	4 - 25	Glass	≈ 10 ²³

2.5 Kinematic viscosity

When Newtonian liquids are tested by means of capillary viscometers such as Ubbelohde or Cannon Fenske, viscosity is determined in units of kinematic viscosity ν . The force of gravity acts as the force driving the liquid sample through the capillary. The density of the sample is one other additional parameter.

Kinematic viscosity ν and dynamic viscosity η are linked:

$$\nu = \frac{\eta}{\rho} \quad [mm^2 / s] \quad [9]$$

ν = Kinematic viscosity

Former units of kinematic viscosity were:

“Stokes” [St] or “centi Stokes” [cSt].

$$1 St = 100 cSt \quad 1 \frac{mm^2}{s} = 1 cSt$$

$$\rho = \text{density} \quad [kg/m^3 = \frac{N \cdot s^2}{m^4}]$$

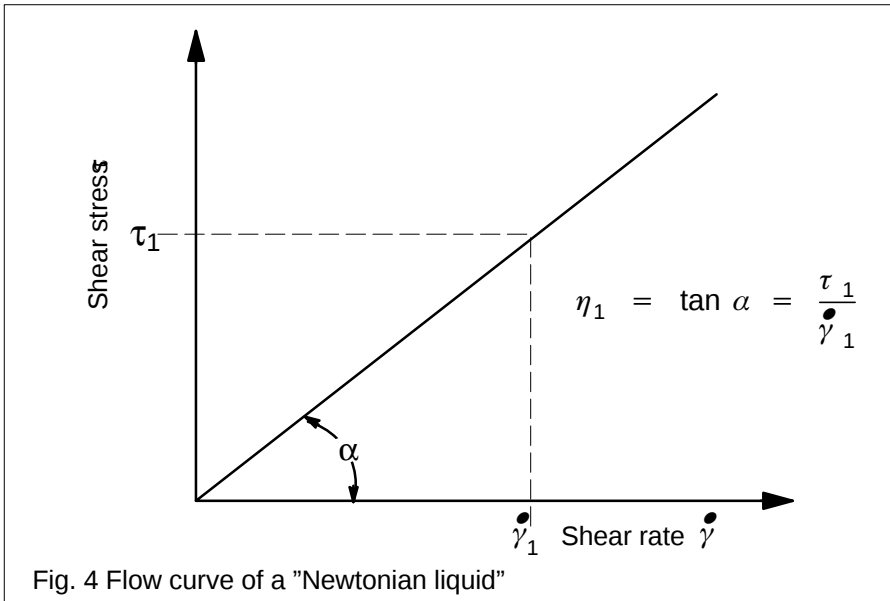
 **Please note:**

“Ford-cup seconds”, “Engler degrees” and “Saybolt or Redwood seconds” are only viscosity related values, which (for non-Newtonian liquids) cannot be converted to the absolute viscosity values of either η or ν .

2.6 Flow and viscosity curves

The correlation between shear stress and shear rate defining the flow behavior of a liquid is graphically displayed in a diagram of τ on the ordinate and $\dot{\gamma}$ on the abscissa. This diagram is called the "Flow Curve".

The most simple type of a flow curve is shown below. The viscosity in equation (2) is assumed to be constant and independent of $\dot{\gamma}$.



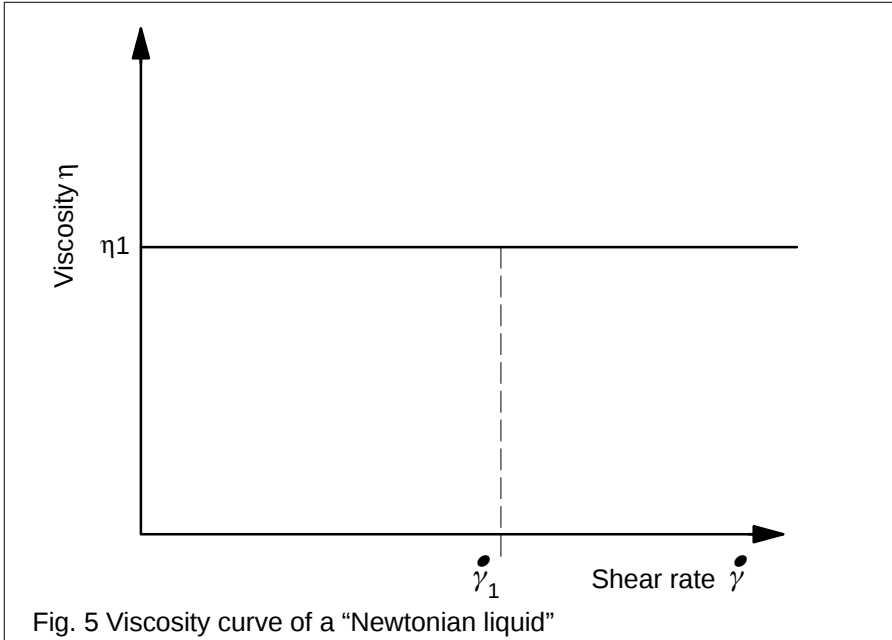
Please note:

In mathematics and physics it is common practice to use the abscissa for the free variable and the ordinate for the resultant. Inasmuch as "controlled rate/CR"-rheometers and viscometers, which preset defined shear rates and then measure the resulting shear stresses, are most common in rheometry, the flow curves shown in this book will use normally the abscissa for the shear rate. In "controlled stress"/CS-rheometers, which are explained in a later chapter, the shear stress is the free variable and the resultant shear rate or deformation is placed on the ordinate. Since almost all rheometers today make use of computers which allow the transformation of the axis definition at any time, flow curves can easily be transformed with shear rate either on the abscissa or on the ordinate. To allow an easy comparison of the results of CS- and CR-rheometers it is common practise to also show CS-flow curves with the abscissa used for the shear rate.

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Another diagram is very common: η is plotted versus $\dot{\gamma}$. This diagram is called the “Viscosity Curve”:



The viscosity curve shown in Fig. 5 corresponds to the flow curve of Fig. 4. Viscosity measurements always first result in the flow curve. It's results can then be rearranged mathematically to allow the plotting of the corresponding viscosity curve. The different types of flow curves have their counterparts in types of viscosity curves.

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2.7 Viscosity parameters

Viscosity, which describes the physical property of a liquid to resist shear-induced flow, may depend on 6 independent parameters:

$$\eta = \text{function of } S, T, p, \dot{\gamma}, t, E$$

“S” This parameter denotes the physical-chemical nature of a substance being the primary influence on viscosity, i.e. whether the liquid is water, oil, honey, or a polymer melt etc.

“T” This parameter is linked to the temperature of the substance. Everybody's experience shows that viscosity is heavily influenced by changes of temperature. As an example: The viscosity of some mineral oils drops by 10% for a temperature increase of only 1°C.

“p” This parameter “pressure” is not experienced as often as the previous ones. Pressure compresses fluids and thus increases intermolecular resistance. Liquids are compressible under the influence of very high pressure – similar to gases but to a lesser extent. Increases of pressure tend to increase the viscosity. As an example: Raising the pressure for drilling mud from ambient to 1000 bar increases its viscosity by some 30%.

“ $\dot{\gamma}$ ” Parameter “shear rate $\dot{\gamma}$ ” is a decisive factor influencing the viscosity of very many liquids. Increasing shear rates may decrease or increase the viscosity.

“t” Parameter “time” denotes the phenomenon that the viscosity of some substances, usually dispersions, depends on the previous shear history, i.e. on the length of time the substance was subjected to continuous shear or was allowed to rest before being tested.

“E” Parameter “electrical field” is related to a family of suspensions characterized by the phenomenon that their flow behavior is strongly influenced by the magnitude of electrical fields acting upon them. These suspensions are called either “electro-viscous fluids” (EVF) or “electro-rheological fluids” (ERF). They contain finely dispersed dielectric particles such as aluminum silicates in electro-conductive liquids such as water which may be polarized in an electrical field. These EVFs may have their viscosity changed instantaneously and reversibly from a low to a high viscosity level, to a dough-like material or even to a solid state as a function of electrical field changes, caused by voltage changes.

EVFs possess a great rheological potential, but in 1994 no commercial large-scale usage in e.g. the automobile or chemical industry has been reported. For literature on ERFs see “references”.

Please note: Lately fluids are investigated which contain particles which can magnetize in an electromagnetic field resulting also in a strong viscosity change. Magneto-rheological fluids (MRF) are technically an alternative to ERF's

2.8 Substances

2.8.1 Newtonian liquids

Please note:

Keeping the concept of the Deborah-number in mind one can better define Newtonian liquids as liquids which exhibit a “Newtonian flow behaviour” under certain conditions of stress or shear rate – see page 4.

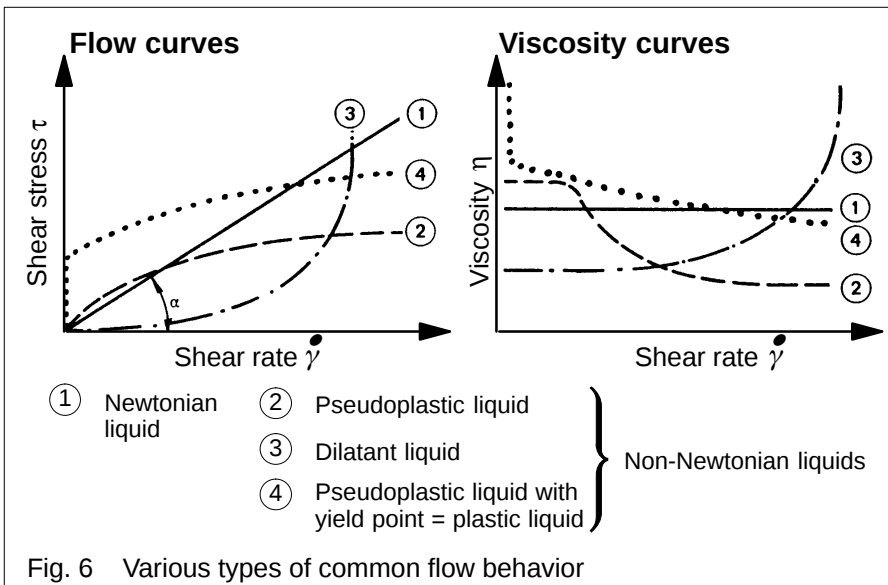
Newton assumed that the graphical equivalent of his equation [2] for an ideal liquid would be a straight line starting at the origin of the flow curve and would climb with a slope of an angle α . Any point on this line defines pairs of values for τ and $\dot{\gamma}$. Dividing one by the other gives a value of η (equation [8]). This value can also be defined as the tangent of the slope angle α of the flow curve: $\eta = \tan \alpha$.

Because the flow curve for an ideal liquid is straight, the ratio of all pairs of τ and $\dot{\gamma}$ -values belonging to this line is constant. This means that η is not affected by changes in shear rate. All liquids for which this statement is true are called “Newtonian liquids” (both curves ① in Fig. 6).

Examples: water, mineral oils, bitumen, molasses, etc.

2.8.2 Non-Newtonian liquids

All other liquids not exhibiting this “ideal” flow behavior are called “Non-Newtonian Liquids”. They outnumber the ideal liquids by far.



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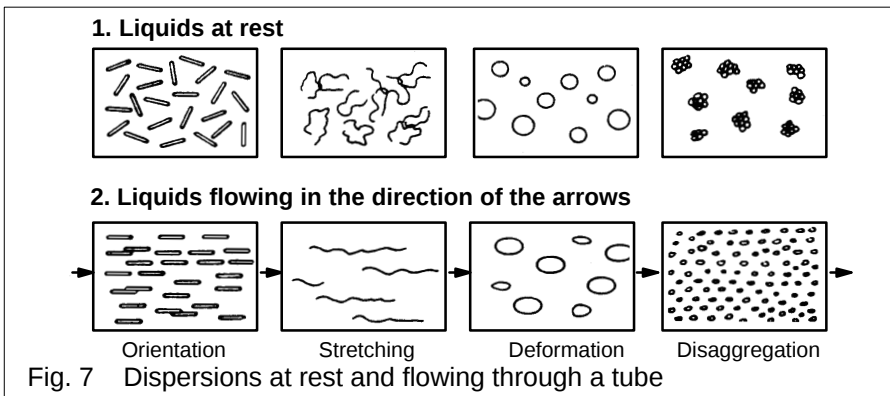
Rheology

A. Liquids which show pseudoplastic flow behaviour under certain conditions of stress and shear rates – often just called “pseudoplastic liquids” (both curves ② in Fig. 6)

Very many liquids show drastic viscosity decreases when the shear rate is increased from low to high levels. In other words ...

- the faster pharmaceutical products are pumped through pipe lines or capillaries,
- the more rapidly paints are sprayed out of a spray gun or brushed onto a wall,
- the harder toothpastes or face creams are squeezed or shaken out of tubes or bottles,
- the more intense a mixing process can be, the faster polymer melts are forced to flow through nozzles of injection moulding machines,

the greater the decrease in the viscosity of these materials will be. Technically this can mean that for a given force or pressure more mass can be made to flow or the energy can be reduced to sustain a given flow rate. Fluids which become thinner as the shear rate increases are called “pseudoplastic”. Very many substances such as emulsions, suspensions, or dispersions of high technical and commercial importance belong to this group. It is worthwhile to indicate some reasons for the shear thinning effect of pseudoplastic materials:



Many liquid products that seem homogeneous are in fact composed of several ingredients: particles of irregular shape or droplets of one liquid are dispersed in another liquid. On the other hand there are polymer solutions with long entangled and looping molecular chains. At rest, all of these materials will maintain an irregular internal order and correspondingly they are characterized by a sizable internal resistance against flow, i.e. a high viscosity.

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With increasing shear rates, matchstick-like particles suspended in the liquid will be turned lengthwise in the direction of the flow. Chain-type molecules in a melt or in a solution can disentangle, stretch and orient themselves parallel to the driving force. Particle or molecular alignments allow particles and molecules to slip past each other more easily. Sphere-shaped particles may be deformed to the shape of “Rugby or American Football balls” i.e. smaller in diameter but longer. Elastically deformable corpuscular cells with a coin-like shape such as red blood cells suspended in plasma, may be reshaped to long thimbles with reduced diameters which means an easier passage through small blood vessels and a higher flow rate. Shear can also induce irregular lumps of aggregated primary filler particles to break up and this can help a material with broken-up filler aggregates to flow faster at a given shear stress.

For most liquid materials the shear-thinning effect is reversible – often with some time lag – i.e. the liquids regain their original high viscosity when the shearing is slowed down or is even terminated: the chain-type molecules return to their natural state of non-orientation, deformed droplets return to ball-shape and the aggregates reform due to Brownian motion.

The rheological literature points out one other possible reason for the shear-thinning of a material: Solvent layers are stripped from dissolved molecules or from particles, which means, that the intermolecular interactions causing resistance to flow become reduced.

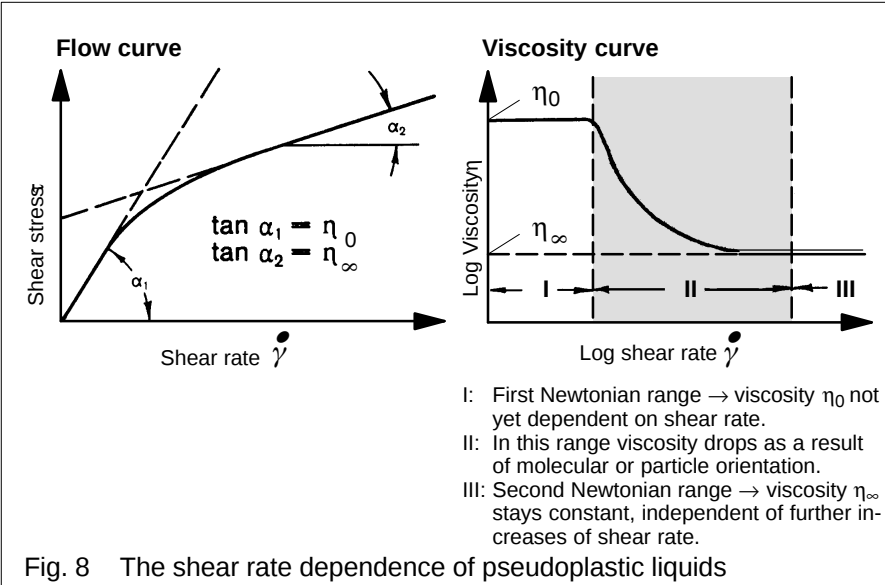
It should be mentioned that the shear-thinning or pseudoplastic flow behaviour of these liquids is not uniform over the range of very low to very high shear rates:

At the low shear rate range the Brownian motion of molecules keeps all molecules or particles at random in spite of the initial effects of shear orientation. At very low shear rates pseudoplastic liquids behave similarly to Newtonian liquids having a defined viscosity η_0 independent of shear rate – often called the “zero shear viscosity”. A new phenomenon takes place when the shear rate increases to such an extent that the shear induced molecular or particle orientation by far exceeds the randomizing effect of the Brownian motion: the viscosity drops drastically. Reaching extremely high shear rates the viscosity will approach asymptotically a finite constant level: η_1 . Going to even higher shear rates cannot cause further shear-thinning: The optimum of perfect orientation has been reached.

In the low and in the high shear rate ranges – called the first and second Newtonian ranges – even the viscosity of non-Newtonian liquids is independent of shear rate: There would be only very small changes for η_0 at $\dot{\gamma} = 0.001 \text{ s}^{-1}$ or $\dot{\gamma} = 0.01 \text{ s}^{-1}$ for most fluids such as polymer melts. Similarly one may expect that the viscosity η_2 at $\dot{\gamma} = 100.000 \text{ s}^{-1}$ would be similar to the viscosity at a shear rate ten times higher – if they could maintain the same mass temperature.

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B. Liquids which show a dilatant flow behaviour – (Curves ③ in Fig. 6)

There is one other type of a material characterized by a shear rate dependent viscosity: “dilatant” substances – or liquids which under certain conditions of stress or shear rate show a dilatant flow behaviour – increase their viscosity whenever shear rates increase. In other words, the more one tries to increase the coating speed for some PVC-plastisols to coat a fabric substrate, the stiffer the coating material becomes. The resistance to flow may become so high that the fabric is torn or even the rolls of the coating calender are broken.

Dilatant flow behavior is found for example in highly concentrated suspensions in which solid particles such as emulsion-PVC are mixed with liquids such as plasticizers to form plastisols. The particles are densely packed and the amount of plasticizer added is just sufficient to fill the void between the particles. At rest or at low coating speeds the plasticizer fully lubricates the particle surfaces and thus allows an easy positional change of particles when forces are applied: this suspension behaves as a liquid at low shear rates. At higher shear rates, particles will wedge others apart causing general volume increases. At this stage the plasticizer's share of the total plastisol volume decreases. Since the plasticizer is no longer sufficient to fill all voids and to keep the PVC-particle surfaces fully lubricated, the plastisol becomes more viscous.

Dilatancy in liquids is rare. Inasmuch as this flow behavior most likely complicates production conditions, it is often wise to reformulate the recipe in order to reduce dilatancy.

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C. Plasticity (both curves ④ in Fig. 6)

It describes pseudoplastic liquids which additionally feature a yield point.

Plastic fluids can be classified with good reasoning to belong to both groups of liquids and solids. They are mostly dispersions which at rest can build up an intermolecular/interparticle network of binding forces (polar forces, van der Waals forces, etc.). These forces restrict positional change of volume elements and give the substance a solid character with an infinitely high viscosity. Forces acting from outside, if smaller than those forming the network, will deform the shape of this solid substance elastically. Only when the outside forces are strong enough to overcome the network forces – surpass the threshold shear stress called the “yield point” – does the network collapse. Volume elements can now change position irreversibly: the solid turns into a flowing liquid.

Typical substances showing yield points include oil well drilling muds, greases, lipstick masses, toothpastes and natural rubber polymers. Plastic liquids have flow curves which intercept the ordinate not at the origin, but at the yield point level of τ_0 .

Please note:

More information about yield values and problems connected with their measurement is given in chapter 8.2.

D. Thixotropy (Curves in Fig. 10)

This term describes a rheological phenomenon of great industrial importance. It calls for some explanation in simplified terms of an otherwise often very complex molecular or particle interaction.

For pseudoplastic liquids, thinning under the influence of increasing shear depends mainly on the particle/molecular orientation or alignment in the direction of flow surpassing the randomizing effect of the Brownian movement of molecules. This orientation is again lost just as fast as orientation came about in the first place.

Plotting a flow curve of a non-Newtonian liquid not possessing a yield value with a uniformly increasing shear rate – the “up-curve” –, one will find that the “down-curve” plotted with uniformly decreasing shear rates will just be superimposed on the “up-curve”: they are just on top of each other or one sees one curve only.

It is typical for many dispersions that they not only show this potential for orientation but additionally for a time-related particle/molecule-interaction. This will lead to bonds creating a three-dimensional network structure which is often called a “gel”. In comparison to the forces within particles or molecules, these bonds – they are often hydrogen or ionic bonds – are relatively weak: they rupture easily, when the dispersion is subjected to shear over an extended period of time (Fig. 9).

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When the network is disrupted the viscosity drops with shear time until it asymptotically reaches the lowest possible level for a given constant shear rate. This minimum viscosity level describes the “sol”-status of the dispersion. A thixotropic liquid is defined by it's potential to have it's gel structure reformed, whenever the substance is allowed to rest for an extended period of time. The change of a gel to a sol and of a sol to a gel is reproducible any number of times. Yoghurts in this context are non-reversible i.e. non-thixotropic fluids because their organic structure can be broken by shear, but once destroyed it will never be rebuilt.

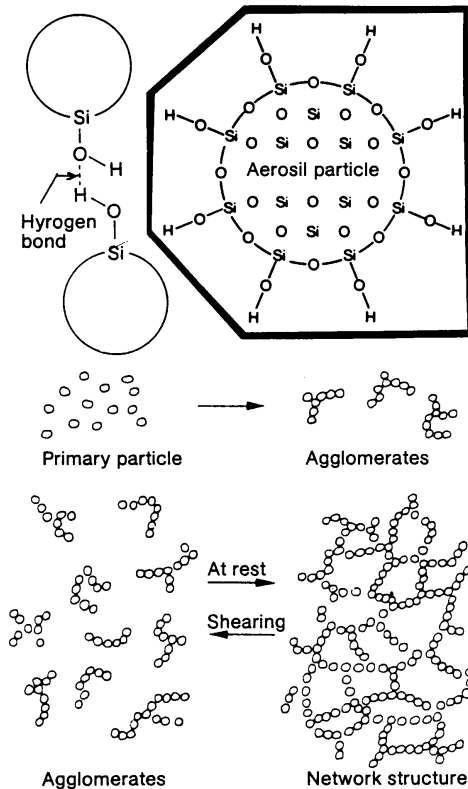


Fig. 9 Particle interaction in thixotropic dispersions

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Fig. 10 describes thixotropy in graphical form. In the flow curve the “up-curve” is no longer directly underneath the “down-curve”. The hysteresis now encountered between these two curves surrounds an area “A” that defines the magnitude of this property called thixotropy. This area has the dimension of “energy” related to the volume of the sample sheared which indicates that energy is required to break down the thixotropic structure

$$A = \tau \cdot \dot{\gamma} \left[Pa \cdot \frac{1}{s} \right] \quad [10]$$

$$\frac{N}{m^2} \cdot \frac{1}{s} = \frac{N \cdot m}{s} \cdot \frac{1}{m^3}$$

$$A = \frac{\text{work}}{\text{shear time}} \cdot \frac{1}{\text{volume}} = \frac{\text{power}}{\text{volume}}$$

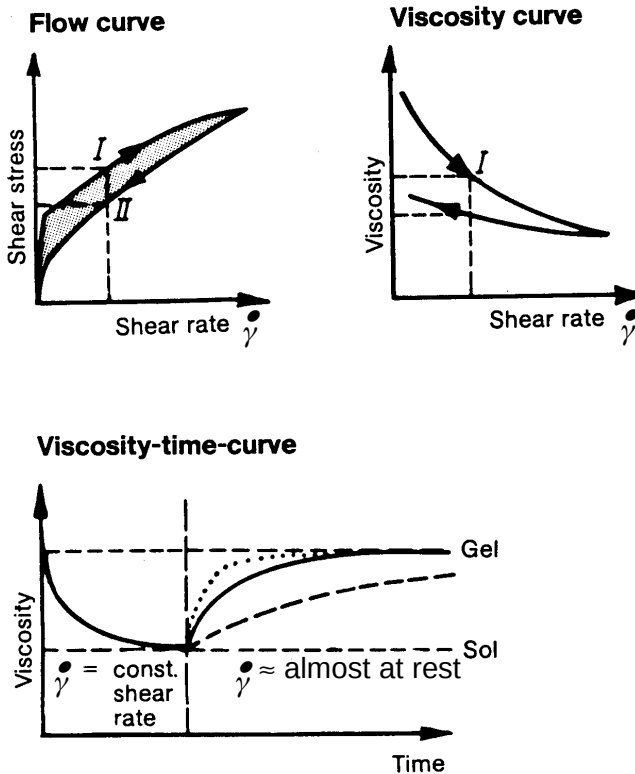


Fig. 10 Diagrams describing thixotropy

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The corresponding viscosity curve indicates what has been pointed out before: viscosity decreases with increasing shear rates as the result of the combined breakdown of thixotropic structure and molecular orientation. When, in the second part of the experiment, the shear rate is continuously decreased, viscosity increases much less than it dropped initially. For the same shear rate there are now two different points I and II. These two viscosity values are caused by a shear history at I being much shorter than at II: If it took 3 minutes to get to point I and 6 minutes to the maximum shear rate, it will be 9 minutes until point II is reached.

The viscosity-time curve marks the two phases of transformation: a gel turns rapidly to a sol when subjected to a constant shear rate. In the second phase the sol converts back to a gel. The rate of this transformation can vary a lot depending mainly on the nature of the thixotropic liquid and its temperature. It may take seconds or minutes to break down a thixotropic structure but in many cases it requires minutes, hours or even months to fully recover the original gel status. While such a full sol-gel-transformation is very time consuming, the rate of partial recovery within the first seconds or minutes after coming to rest can be quite remarkable: 30 to 50% of the viscosity may be recovered within this short period. The early rate of recovery is often of great technical importance.

Thixotropy is a very important feature in paints, foodstuffs, cosmetics, pharmaceuticals, and other products of industrial importance.

Two examples:

- brushing paints onto vertical walls breaks down their thixotropic structure and allows them to be spread thinly and easily. Once applied to the wall the paint must recover its gel structure as fast as possible to prevent the paint layer from sagging off the wall.
- children are fed cough syrup by the spoon. This sort of medicine is often a dispersion of the drug diluted in a sugary syrup so that children like to take their medicine which otherwise may taste bad. The drug being of higher density than the syrup, tends to sink during the weeks or months before usage to the bottom of the bottle. To prevent this separation the medicine is reformulated with additives which make the syrup thixotropic. During processing in large mixers all the ingredients are kept uniformly dispersed. The cough remedy is in its sol state in those mixers and pipelines until it comes to rest after having been filled rapidly into the bottles. Now the potential to recover a thixotropic structure rapidly means that in a thickening syrup, sedimentation of components of higher density cannot take place any longer. With these new types of cough syrups problems which occurred with non-thixotropic formulations have been overcome: contrary to the instructions on the bottle, mothers often forgot to shake the contents thoroughly and consequently first fed their children a useless “medicine” additive for days, and then the pure drug all at once.

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E. Liquids which show a rheopectic – anti-thixotropic – flow behavior

It is common to call them for short: rheopective liquids. They are characterized by a viscosity increase related to the duration of shear. When these liquids are allowed to rest they will recover the original – i.e. the low – viscosity level. Rheopective liquids can cycle infinitely between the shear-time related viscosity increase and the rest-time related decrease of viscosity. Rheopexy and thixotropy are opposite flow properties. This can also be seen in the sense of the hysteresis of the flow curve, i.e. where the up-curve is positioned in relation to the down-curve. Rheopective liquids show a counter-clockwise sense: The down-curve comes back above the up-curve. Thixotropy is a very common behavior for many liquids whereas true rheopexy is very rare indeed.

At this point the reader should be warned: in quite a number of cases when the hysteresis of the flow curve shows a counter-clockwise sense, the material is not really rheopectic.

- A viscosity increase as the result of an extended duration of shear can be noticed whenever the liquid during that period changes either in its physical or its chemical nature – it may gel, cure or lose solvent by evaporation. In all of these cases the changes of the liquid are non-reversible, i.e. the original low viscosity can never be reached again just by allowing the liquid to rest. While for really rheopectic liquids the hysteresis flow curves of several cycles will be identical, the hysteresis curves of the gelling or curing liquids will change even more with each new cycle.
- Flow curves and the magnitude of the hysteresis can also be influenced by the chosen rate of programmed rotor speed increases and decreases: If not enough time is allowed to reach a steady-state for the shear stress/shear rate interdependence then the shear rate will increase already before the corresponding shear stress value has been attained.

For each sample and any fixed rotor speed n , i.e. a defined value of shear rate $\dot{\gamma}$, the instrument will measure the corresponding true shear stress τ . If the rotor speed and thus shear rate is subjected to programmed changes, the corresponding values of shear stress may only be indicated with some time lag. The higher the rate of rotor speed change and the higher the viscosity of the sample is, the more the time lag increases.

As a result of this time lag, the actual up-curve will be below and the actual down-curve will be above the true flow curve. Thus, a high rate of rotor speed change for a high viscosity liquid can simulate a rheopectic flow behaviour which, in fact, does not exist.

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Please note:

Having listed and explained the 6 main parameters that might influence viscosity (S, T, p, $\dot{\gamma}$, t and E), one can draw one important conclusion for the measurement of viscosity:

In order to define the viscosity as a function of one parameter the other parameters must be kept well defined and constant during the measurement.

Example:

When 5 different dispersions, e.g. salad dressings, have to be tested and compared with respect to their viscosity, rigid test conditions have to be enforced:

a) Temperature T

The temperature of the samples must be controlled so that the specific temperature is maintained within limits of at least $\pm 0.1^\circ\text{C}$. The jacketed sensors of rotational viscometers can therefore be connected to a constant temperature thermal liquid bath and circulator for this purpose. By means of the temperature controlled liquid, the sample can be heated or heat can be removed when frictional heat is generated as the result of testing.

b) Pressure p

One may assume that such a dispersion is always produced and consumed at ambient pressure. It therefore makes sense to test the samples in this case in open sensors.

c) Shear rate $\dot{\gamma}$

Assuming that salad dressings show a highly non-Newtonian flow behavior and their viscosity therefore depends heavily on the shear rate, one should test all the samples at the same fixed shear rate or compare the complete flow curves.

d) Shear history t

If the samples are thixotropic – and most likely they will be – then one may want to test them always in the fully sheared-down sol-condition. Alternatively one has to follow a tight time schedule, i.e. always measuring after 2, 5 or 10 minutes of shearing or after 1, 2 or 7 days of resting.

e) Electrical field E

In EVF-dispersions characterized by the nature and percentage of their dielectrical particles, the electrical field acting on the samples placed into a special sensor system must be kept constant to allow a meaningful comparison of similar EVF-fluids.

2.9 Boundary conditions or measuring constraints of rheometry.

The mathematical treatment of the physical problem of a fluid being deformed under the influence of shear forces leads to very complex differential equations which in their general form cannot be solved. The problem can only lead to an acceptable mathematical solution when test conditions are kept within restrictions (in mathematical terms, boundary conditions). Newton's law of rheometry [2] is only valid within the framework of these restrictions. The measurement of viscosity requires test conditions providing:

2.9.1 Laminar flow

The applied shear must lead only to laminar flow. Inasmuch as laminar flow prevents exchange of volume elements between layers, samples must be homogeneous to start with. A homogenizing effect on heterogeneous samples during testing cannot be expected or permitted.

On the other hand this requirement prevents using a mixer as a sensor for the measurement of absolute viscosity. Mixers as processing machinery have their rotors and bowls designed to create as much turbulent flow as possible to inter-mix all components thoroughly. Much more energy is required to maintain turbulent flow than simply maintaining laminar flow. Thus the measured torque is no longer proportional to the true viscosity of a sample. Allowing turbulent flow in viscosity measurements would introduce errors of 50%, 100% or more.

2.9.2 Steady state flow

In Newton's law of rheometry [2] the shear stress applied is correlated to the shear rate. The shear stress meant was the one that was just sufficient to sustain a constant flow rate. The additional energy required to accelerate or to decelerate the flow cannot be accounted for in the equation [2].

2.9.3 No slippage

The shear stress applied (see Fig. 3) must be transmitted from the moving plate across the liquid boundary layer into the liquid. In case that adherence between the moving plate and the liquid is insufficient to transmit the shear stress – the moving plate slips above the non-moving liquid sample – any test results will be meaningless. Problems with slippage often arise with fats and greases.

2.9.4 Samples must be homogeneous

This requirement means that the sample must react to shear uniformly throughout. If samples are dispersions or suspensions then all ingredients, droplets or bubbles have to be very small with respect to the thickness of the liquid layer sheared, i.e. they have to be homogeneously distributed.

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In rheometry really homogeneous samples are rare. If dispersions are considered homogeneous because every small volume element contains an identical share of all the ingredients, then problems can still occur when the increasing shear encountered during the measurement leads to phase separation. In such a case a dispersion such as tooth paste may separate into a thin liquid layer at the boundary to the rotor and the remainder of the sample becomes stagnant and solid within the rest of the gap between the rotor and the outer cylinder. Under these conditions viscous flow does only exist in the very thin liquid layer of unknown thickness and the test results are not open for any rheological interpretation once this phase separation has occurred. Just waiting at zero rotor speed does not reconstitute the original sample. A new test with a new sample must be programmed to stop before the shear rate reaches this limit leading to phase separation.

2.9.5 No chemical or physical changes in the sample during testing

Changes due to chemical processes such as hardening or degradation of polymers or physical transformations as they are found in i.e. PVC-plastisols with their particle-plasticizer-interactions would be secondary influences on viscosity. They must be avoided in normal rheometry apart from those cases when just these influences are the main target of research.

Keeping all parameters mentioned above constant, tests may be carried out to follow for example the chemical processes of curing or gelling of polymers by plotting the resulting viscosity changes with respect to time. This can be a very meaningful, relative rheological test.

2.9.6 No elasticity

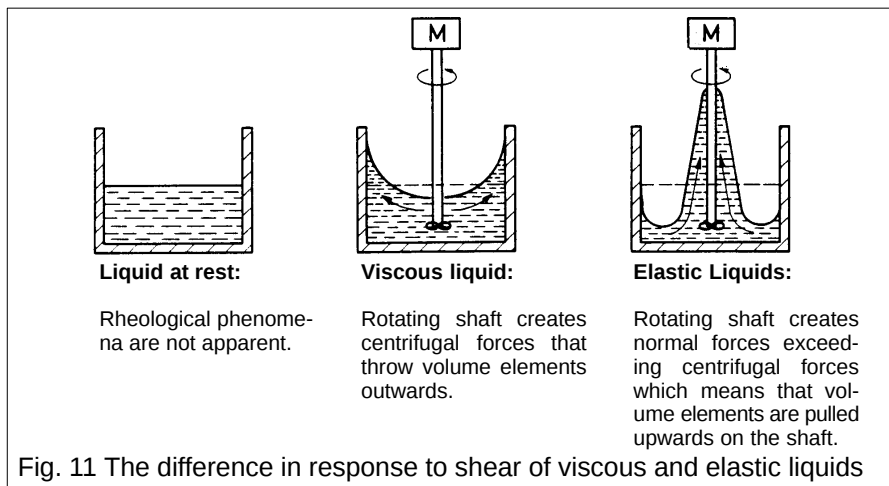


Fig. 11 The difference in response to shear of viscous and elastic liquids

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Liquids may show the following phenomena (see Fig. 11): Two different unpigmented, transparent liquids such as water or rubber polymer solutions at rest cannot be optically differentiated. But stirred fast by a rotor they respond differently: the water is thrown outwards and upwards on the container wall by the centrifugal force that rotation creates while for the other elastic liquid, normal stresses appear surpassing the shear stresses, which strangle the liquid upwards on the rotor shaft.

Fluid samples should be purely viscous when making use of the simple law of rheometry. The total energy input in steady state flow for a sample should lead to a well documented flow and finally to a total conversion of shear energy into shear heating.

If a sample is visco-elastic then some percentage of any shear energy input during unsteady processes is stored elastically and temporarily and only the unknown rest will induce flow. Under these conditions the viscosity-related direct correlation between the known amount of energy input and resulting flow is no longer valid. Simple viscometry will provide very erroneous results for this class of fluid.

Very many samples such as polymer melts or polymer solutions and also very many dispersions show both a viscous and an elastic response to shear stresses or shear rates. Additionally the ratio of one response to the other changes with the variation of shear rate.

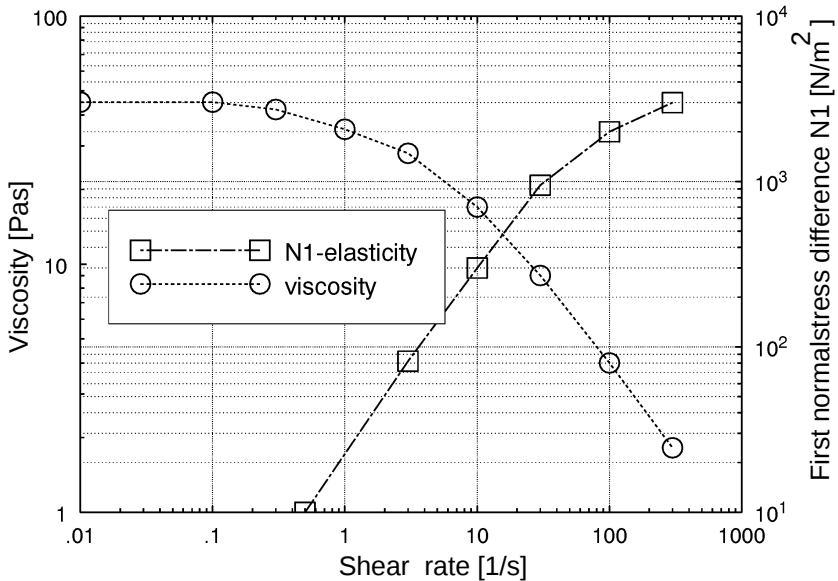


Fig. 12: Viscosity and N1 (Elasticity) as a function of shear rate

While at very low shear rates all fluids are predominantly viscous and the elastic component of their flow behaviour may be neglected, the situation is totally reversed at high shear rates. Fig. 12 indicates that elasticity as characterized by the first normal force difference increasingly exceeds the viscosity at higher shear rates.

Investigating the full scope of visco-elastic behavior calls for the use of rheometers technically much more sophisticated with respect to the simpler viscometers. They will be dealt with in detail in chapter 4.

The property of elasticity in visco-elastic fluids cannot be eliminated as such. But one may find test conditions for viscometers and specifically shear rates low enough to keep the elastic response to shear insignificant. The viscosity test results are then useful enough to differentiate rheologically between similar samples as required for quality control. In the case of an investigation of an unknown sample with regard to its visco-elasticity, it is good practice to first use a sophisticated rheometer and use it to examine the shear rate and time effects on both viscosity and elasticity and then choose test conditions suitable for simpler viscometers.

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2.10 Absolute rheometry/viscometry

Rheometers are defined as “absolute rheometers” if the measurement of viscosity can be traced to the measurement of the test results in the “absolute units of physics”:

Forces	→	In units of “Newton” [N]
Dimensions of the sensor system	→	In units of “meters” [m]
Time intervals	→	In units of “seconds” [s]

Viscosity is then defined in the resultant unit of “Pascal · seconds” [Pa·s]

$$\eta = \frac{N}{m^2} \cdot s = \frac{force}{length^2} \cdot time = Pa \cdot s$$

Requirements for absolute viscosity measurement are:

- The samples tested must be subjected to a flow pattern that lends itself to a mathematical evaluation, i.e. the flow realized in the sensor system of a rheometer must belong to one of the 4 types as indicated in Fig. 2. Shear stresses and shear rates either at the walls of the sensor system or at representative points across the width of the substance sheared must be open for exact calculation.
- Test conditions chosen must take into account the limits as given by the boundary conditions mentioned.

One important benefit of absolute rheometry is that the test results are independent of the particular type or make of rheometer or viscometer used. This is important enough for testing Newtonian liquids but it is essential for defining non-Newtonian flow properties.

Absolute rheometry data can be compared easily between laboratories worldwide. They are an accepted common basis in discussions between suppliers and users related to the rheological behavior of semi-solids and all visco-elastic fluids.

3. Types of Rheometers/Viscometers

3.1 Rotational rheometers/viscometers

3.1.1 Comparing the different design principles

The principle of rotational rheometers with coaxial cylinder-, cone-and-plate- and parallel-plate sensor systems allows the design of excellent and versatile absolute rheometers. The range of rotational rheometers and viscometers on the world market varies widely in sophistication and price. The rheological criteria and boundary conditions mentioned before are used to grade types of instruments and explain design features and resulting areas of application.

One might imagine that the coaxial cylinder sensor systems for rotational rheometers/viscometers result from bending both flat plates of the Newton's parallel-plate-model (see Fig. 3) into an inner and outer cylinder. A liquid sample filling the annular gap between the two cylinders can be exposed to shear for any length of time. Conditions as in Fig. 2b will lead to laminar flow, and allow a mathematical treatment of measured data delivering test results of shear stresses, shear rates and viscosity in the appropriate physical units. The same can be said for cone-and-plate- and for parallel-plate-sensor systems, which have special application areas.

Two basic alternatives are open to turn the above geometries into an absolute rheometer/viscometer, which can provide:

- A)** a controlled stress input and determine the resulting shear rate: They are named "controlled stress- or CS-rheometers" or ...
- B)** a controlled shear rate input and determine the resulting shear stress: They are named "controlled rate- or CR-rheometers".

Some modern rheometers have the potential to work in both test modes. But there are two other additional design differences for rheometers:

1.) Searle- and 2.) Couette-measuring systems

A1) CS-rheometer with a Searle type measuring system combined with coaxial cylinder-, cone-and-plate, or parallel-plate sensor systems:

The outer cylinder – cup – is stationary allowing an easy temperature control of the jacketed cup normally connected to an "external thermal liquid, constant temperature bath and circulator" – most of the time just called "circulator".

The inner cylinder – rotor – is driven by a special motor "M" for which defined torque values may be preset: an electrical power input results in linearly related torque values on the motor shaft. The resistance of the sample placed

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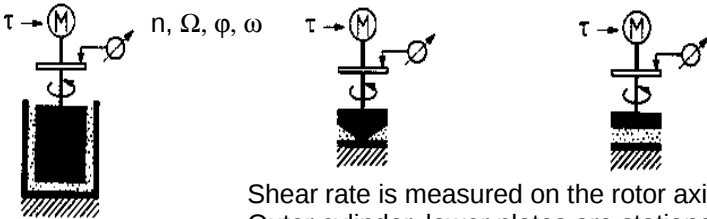
Rheology

A. Controlled Stress (CS) Rheometer

Torque/Shear stress assigned and strain/strain rate measured.

Searle type sensor systems: Rotor rotates

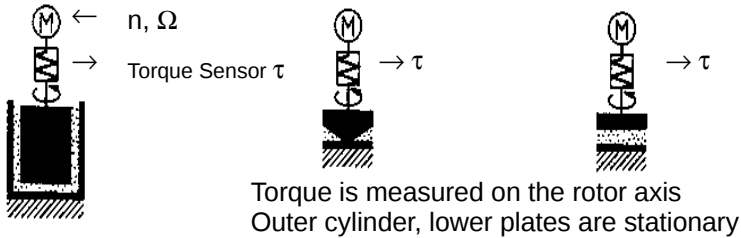
Can be converted to allow CR-mode



Controlled Rate (CR) Rheometer / Viscometers

Shear rate assigned and shear stress measured.

B1. Searle type sensor systems: Rotor rotates



B2. Couette type sensor systems: Outer cylinder or lower plates rotate

Torque is sensed on the inner, non-rotating cylinder or cone

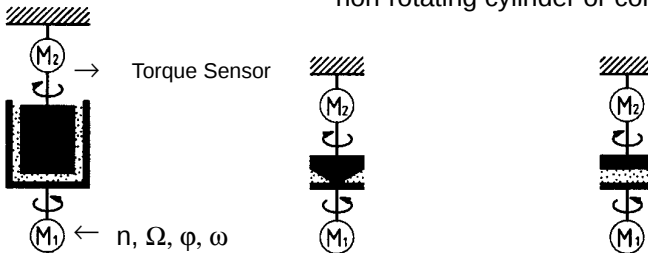


Fig. 13 Types of rotational rheometers

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inside of the sensor system against the applied torque or shear stress will allow the rotor to rotate only at a speed – shear rate – that inversely correlates to the viscosity of this sample. The rotor speed “ n ” and the strain position ϕ is measured by means of an optical sensor which divides a 360° revolution into 1000000 increments and is therefore able to detect extremely small angular deflections of the rotor.

“Searle” in this context means that torque input and resulting rotor speed act on the same rotor shaft axis. The sensor systems are designed so that torque data can be mathematically transformed to shear stress and the rotor speed to shear rate.

The sensor systems can be modified so that the outer cup is exchanged for a stationary lower plate and the inner cylinder for either a rotating cone or an upper plate. A special modification of such a lower plate may contain “normal force sensor” to measure in addition to the viscosity also the elasticity of visco-elastic fluids.

Viscosity measurement now means: Preset a given value of torque, measure the resulting rotor speed and evaluate them for shear stress and shear rate to provide the corresponding value of the viscosity.

Rheometers constructed according to this design have the potential for additionally measuring the visco-elastic properties of soft-solids and fluids, thus bringing them into the top-class of rheometers.

B1) CR-rheometer with a Searle-type measuring system combined with coaxial cylinder-, cone-and-plate, or parallel-plate sensor systems.

The inner cylinder – rotor – is driven by a motor “M”. Its speed is controlled for constant or programmed rotor speeds while the other cylinder – cup – is held at rest. The cup is jacketed for an accurate temperature control of samples. The driven inner cylinder forces the liquid in the annular gap to flow. The resistance of the liquid being sheared between the stationary and rotating boundaries of the sensor system results in a viscosity-related torque working on the inner cylinder which counteracts the torque provided by the drive motor. A torque detector – normally a spring that twists as a result of the torque applied – is placed between the drive motor and the shaft of the inner cylinder. The twist angle of the torque spring is a direct measure of the viscosity of the sample. While years ago viscometers were equipped with torque springs which were twisted up to 90° – soft springs –, nowadays twist angles of 0.5° – rigid springs – are more common in viscometers. “Searle” again means that both the drive on the rotor and the torque detector act on the same rotor axis.

An easy variation of the geometry of the sensor systems – coaxial cylinder, cone-and-plate and parallel-plate sensor systems – allows a versatile usage of this type of rheometer for the measurement of fluids of either medium or very high viscosity. Searle type in comparison to Couette rheometers run into more problems with low viscosity liquids at high shear rates since under those conditions the laminar flow may cause turbulence resulting in erroneous results.

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Designed for the low to medium price range, these instruments are the most common type of rotational viscometers on the world market for quality control purposes.

B2) CR-rheometer with a Couette measuring system and sensor systems of coaxial cylinder-, cone-and-plate- or parallel-plate design.

The outer cylinder driven by the motor “M1” rotates at a defined speed. It’s temperature control presents technical and relatively costly problems. It forces the liquid sample in the annular gap to flow. The resistance of the liquid against being sheared transmits a viscosity related torque onto the inner cylinder, which would induce it also to rotate. This torque is measured by determining just what counteracting torque is required to hold the inner cylinder at a stand-still.

The “Couette” design now means that the drive acts on the outer cup while the viscosity-related torque is measured on the shaft of the inner cylinder – the other element of the sensor system.

Instead of a spring as a torque sensing element as mentioned for B1 a secondary motor “M2” acting on the shaft of the inner cylinder or cone is controlled to provide that much of a counter-torque to keep the inner cylinder, the upper cone or plate from starting to move. In this compensatory test method the wattage for the secondary motor M2 is the viscosity-related test signal.

Couette type measuring systems maintain laminar flow even when low viscosity liquids are tested at high shear rates and it is in this area that they surpass Searle-type CR-rheometers. Their additional advantage is noteworthy inasmuch as the B2-rheometers can be designed to allow the testing of visco-elastic fluids with respect to their viscous and elastic properties. This is done either by measuring the response of samples to sinusoidal oscillations of the driven member of the sensor system or by determining the elasticity-related normal forces which tend to separate the cone from the plate or upper plate from the lower plate during steady shear.

Rheometers with a Couette measuring system may be top-class, versatile instruments providing insight into the visco-elastic nature of fluids.

For identical non-thixotropic liquids both the CS- and CR-rheometers with either Searle- and Couette-measuring systems will provide identical flow- and viscosity curves.

Assuming for Searle- and Couette measuring systems very small gap sizes and equal values of rotational speed “ v ” on either the inner or the outer cylinder wall, the viscosity “ η ” of a Newtonian liquid is constant across the annular gap and equal for both measuring systems.

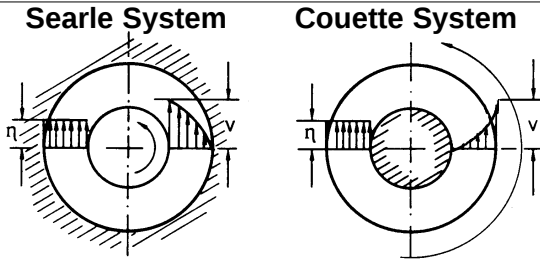


Fig. 14 Velocity and viscosity in Searle and Couette sensor systems

3.1.2 Comparison of CS- and CR-rheometers

One should note the important differences between CS- and CR-rheometers when testing visco-elastic fluids and especially those which are known for their yield values giving them some solid and some liquid shear response:

a) *Most CS-rheometers are designed to provide a much higher sensitivity to differentiate better between similar samples at very low values of shear rate, at which simpler viscometers cannot provide significant data.*

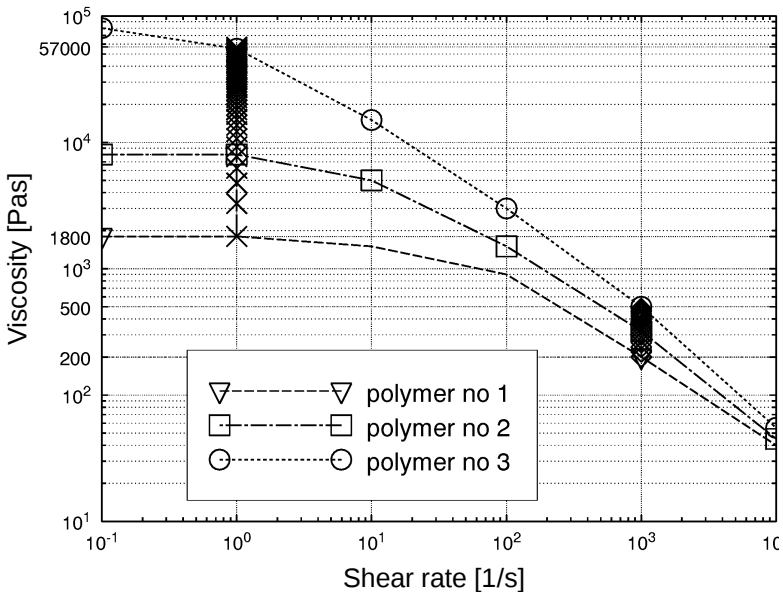


Fig. 15: Viscosity curves of 3 PMMA melts at 220°C

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Gleissle {4} has made people aware of the following problem:

Different grades of polymer melts differing in their molecular structure provide viscosity/shear rate-curves which are much closer together at high shear rates than at low shear rates. A typical example of such a flow behavior is given in Fig. 15, in which the viscosity curves of 3 PMMA-melts tested in a capillary rheometer are plotted. Inspecting these three curves will lead to the conclusion that it is preferable to test not only these PMMA-melts but generally similar polymer melts at low shear rates to best differentiate between them. This statement is supported by both the viscosity ratios and differences at high and low shear rates:

Polymer no. 1 $\rightarrow \eta_1$

Polymer no. 3 $\rightarrow \eta_3$

The ratios η_3/η_1 at $\dot{\gamma} = 1$ 1/s :
at $\dot{\gamma} = 1000$ 1/s:

$\eta_3/\eta_1 = 57000/1800 = 31.6$
 $\eta_3/\eta_1 = 500/200 = 2.5$

The differences $\eta_3 - \eta_1$ at $\dot{\gamma} = 1$ 1/s:
at $\dot{\gamma} = 1000$ 1/s:

$\eta_3 - \eta_1 = 57000 - 1800 = 55200$
 $\eta_3 - \eta_1 = 500 - 200 = 300$

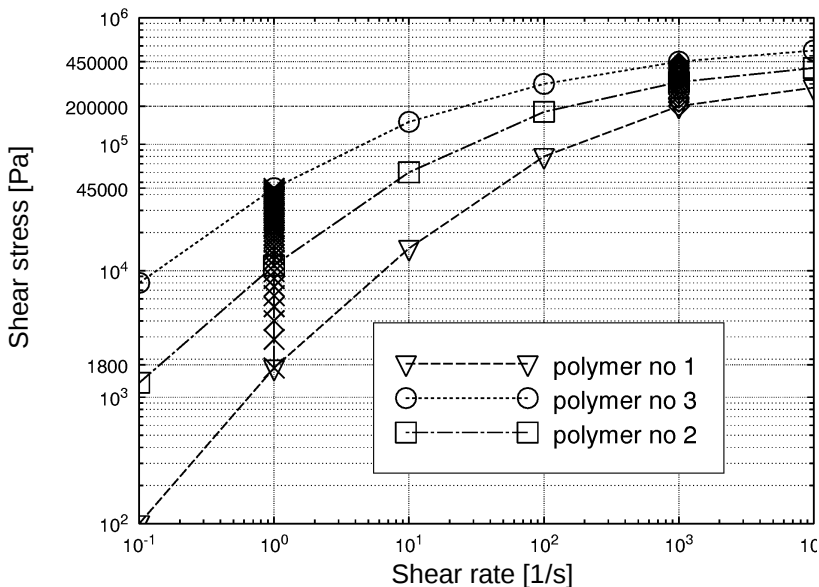


Fig. 16:

Flow curves of 3 PMMA melts at 220°C

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One has to keep in mind that the viscosity is not measured directly but is deduced from the actually measured interdependence of shear stress and shear rate— Fig. 16.

One can similarly list the different ratios and differences of the shear stress data at low and high shear rates:

$$\begin{array}{ll} \text{The ratios } \tau_3/\tau_1 \text{ at } \dot{\gamma} = 1 \text{ 1/s:} & \tau_3/\tau_1 = 45000/1800 = 25 \\ \text{at } \dot{\gamma} = 1000 \text{ 1/s:} & \tau_3/\tau_1 = 450000/200000 = 2.25 \end{array}$$

The ratio of the shear stresses is again larger for the low shear rate level. **But** this is no longer true for the shear stress differences:

$$\begin{array}{ll} \text{The differences } \tau_3 - \tau_1 \text{ at } \dot{\gamma} = 1 \text{ 1/s:} & \tau_3 - \tau_1 = 45000 - 1800 = 43200 \\ \text{at } \dot{\gamma} = 1000 \text{ 1/s:} & \tau_3 - \tau_1 = 450000 - 200000 = 250000 \end{array}$$

The magnitude of the difference is much larger at high in comparison to low shear rates and this leads to the conclusion that the resolution of viscosity measurements is better in the high shear rate region.

The above shown flow curves cover a shear rate range of 5 decades. They are the combined results of tests with several capillary dies of varying geometries because the range of a single die is not more than about 2 decades. At the lower end of such a range the percentage of errors amounts to 10% or more – see chapter 6 – on the significance of test results. The shear stress of PMMA no.1 at the shear rate of $\dot{\gamma} = 0.1 \text{ 1/s}$ is only 100 Pa in comparison to 200 000 Pa at $\dot{\gamma} = 1\,000 \text{ 1/s}$. No capillary rheometer will provide significant data at shear rates much below $\dot{\gamma} = 1 \text{ 1/s}$ because there are no pressure sensors available on the commercial market that are sufficiently sensitive to determine pressure differences at extremely low flow rates while being sturdy enough to cope with pressures of some 500 bar in the starting phase of the test and at high flow rates.

If one wants to make use of the wide spread of viscosity data of several polymer melts at low and very low shear rates to get a clear insight into their molecular structure, one cannot hope to get significant results from capillary rheometers. Only rheometers making use of a totally different type of sensor such as CS-rheometers can reach into a shear rate range which is not open for other types of rheometers.

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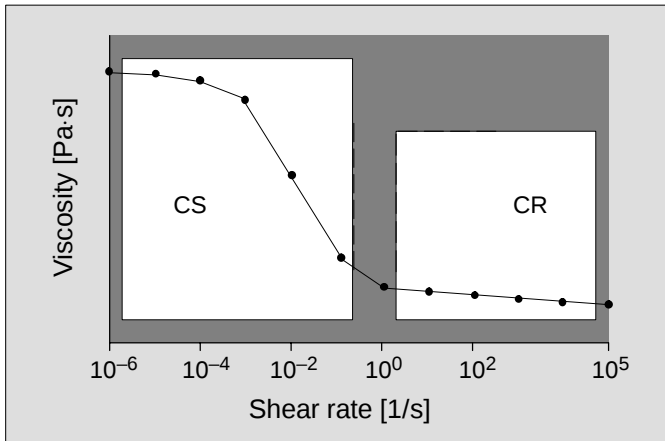


Fig. 17 Schematic shear rate ranges of different measuring modes

The design of CS-rheometers such as the HAAKE Rheostress RS100 which features an air bearing for the rotor shaft extends the usable shear rate range to $\dot{\gamma} = 10^{-4}$ or even 10^{-6} 1/s at which still significant torque/shear stress data and subsequently viscosity data can be determined. The lowest shear rate of CS-rheometers extends many decades below the ranges that may be reached by CR-rheometers – Fig.17. To a certain extend the shear rates of both the CS- and CR-rheometers can overlap when using the full range of their sensor systems. But when it comes to testing at high shear rates the capillary rheometers can out-match rotational rheometers with cone-and-plate or parallel-plate sensor systems.

b) CS- in comparison to CR-measurements differentiate better highly non-Newtonian fluids.

Very many polymer melts and dispersions are highly non-Newtonian, i.e. increases in shear rate do not lead to proportional increases in the shear stress as is the case of Newtonian liquids.

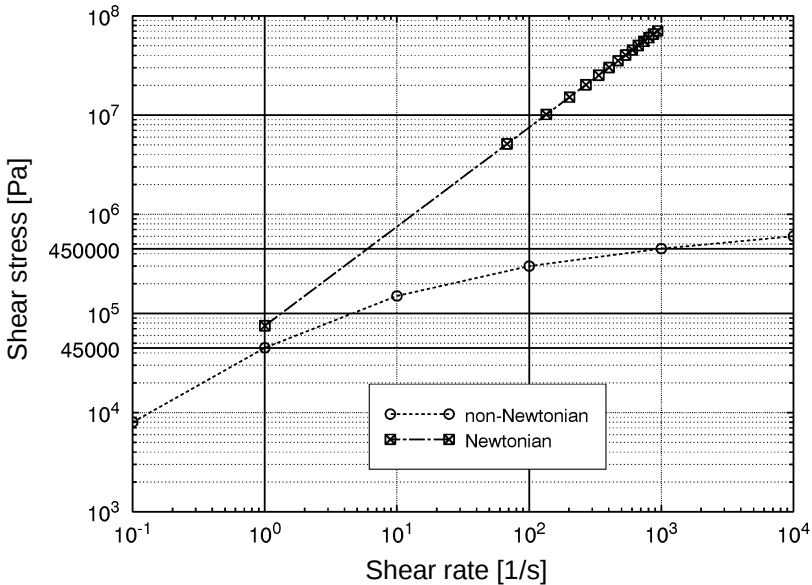


Fig. 18 Flow curves of a Newtonian and a non-Newtonian liquid

In Fig.18 a 3-decade increase in shear rate increases the shear stress also by 3 decades for the Newtonian liquid while it only results in a single decade increase of shear stress for the non-Newtonian PMMA melt:

$\tau = 45000$ to 450000 Pa.

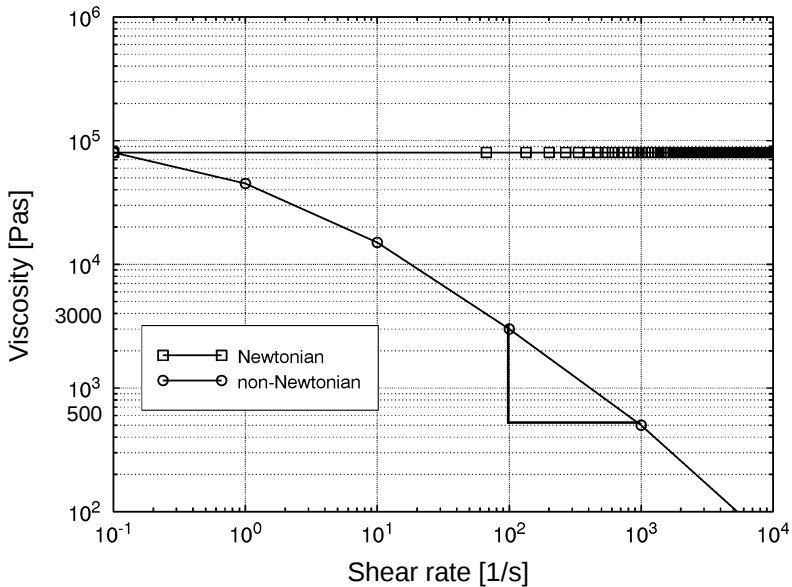


Fig. 19 Viscosity curves of a Newtonian and a non-Newtonian liquid

With respect to the viscosity curves (see Fig.19) the Newtonian liquid is represented by a parallel to the shear rate abscissa: viscosity is independent of shear rate, while the PMMA-melt viscosity decreases from $\eta=3\,000$ to 500 Pas (100 to 16%) for a 1-decade shear rate increase.

When measuring the viscosity of Newtonian liquids the results as such and the measuring resolution are equal for CS- and CR-rheometers. This statement is no longer valid when non-Newtonian liquids are rheologically tested.

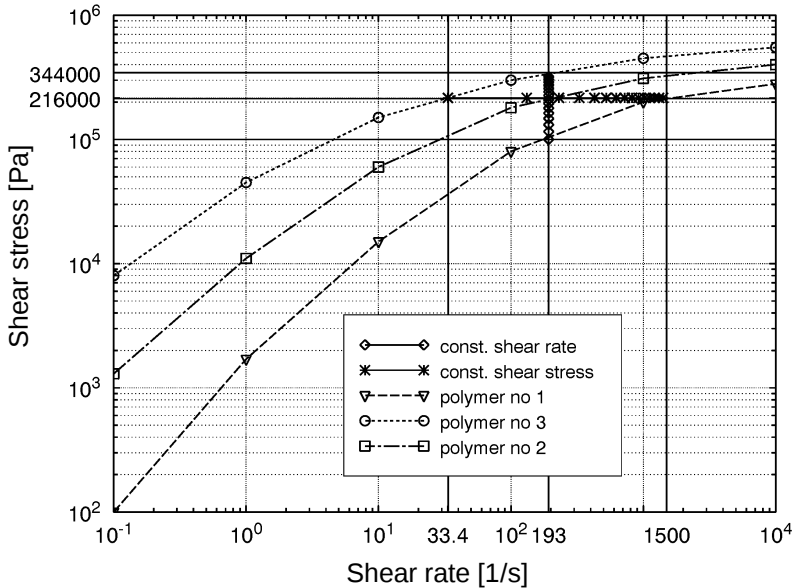


Fig. 20 Flow curves of 3 PMMA melts at 220°C

Fig. 20 compares the resolution of the 3 PMMA-flow curves at a constant shear rate of $\dot{\gamma} = 193$ (1/s) and at a constant shear stress of $\tau = 216\,000$ Pa.

PMMA3/PMMA1 at $\dot{\gamma} = 193$ 1/s = $344\,000/100\,000 = 3.4$
 PMMA1/PMMA3 at $\tau = 216\,000$ Pa = $1500/33.4 = 45$

Constant Stress rheometers are much better – here, more than tenfold – at differentiating between the three melts than **Constant Rate** rheometers and this differentiation becomes even better the more the slope α of the flow curves decreases – the more the samples deviate from Newtonian flow behavior. This slope can be determined by means of regression calculations using the Ostwald-de Waele or “power-law” equation – Fig. 21:

$$\tau = k \cdot \dot{\gamma}^n \text{ - the computer prints: } y = a \cdot x^b.$$

k = consistency as a viscosity related constant,

$n(b)$ = exponent (flow index) = $\tan \alpha$ = slope of the log–log flow curve.

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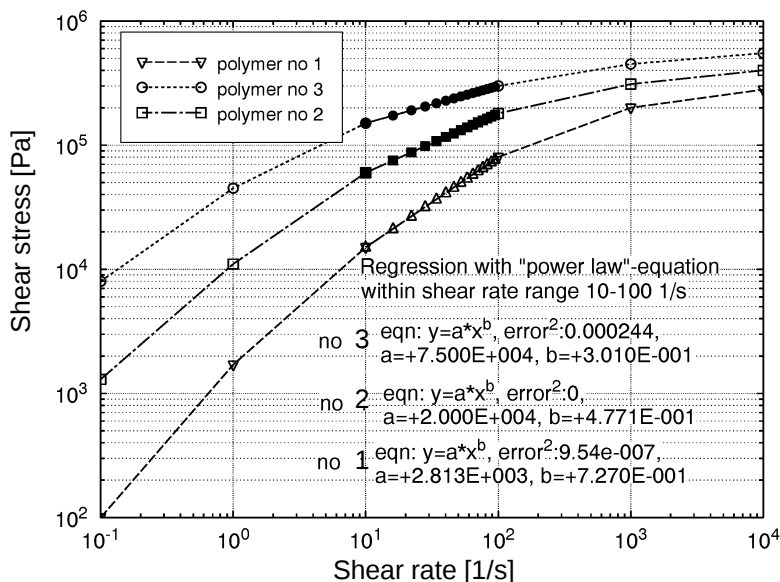


Fig. 21 Flow curves with segmented regression of 3 PMMA grades at 220°C

This exponent equals $n = 1$ for Newtonian liquids and decreases the more the sample becomes non-Newtonian. For the three samples, mean values of slopes $n = \tan \alpha$ are given for the shear rate range:

$\dot{\gamma} = 10-100 \text{ 1/s}$:

$n(\text{PMMA1}) = 0.301$
$n(\text{PMMA2}) = 0.477$
$n(\text{PMMA3}) = 0.727$

The advantage of CS-testing becomes even more apparent when samples are tested with exponents below $n = 0.3$.

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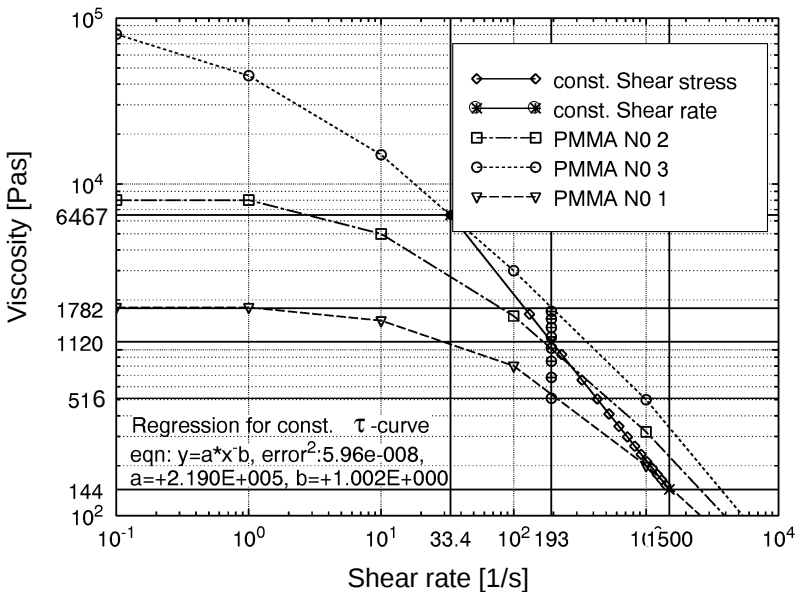


Fig. 22 Viscosity curves of 3 PMMA melts at 220°C

The viscosity curves (see Fig. 22) for the 3 PMMA-melts show a similar differentiation pattern: constant shear rates are defined by parallels to the ordinate. A constant shear stress $\tau = 216\,000\text{ Pa}$ is marked by a line with a slope of 45° ($\tan \alpha = -1$), which intersects with the PMMA3-curve at $\eta = 6\,467\text{ Pa}\cdot\text{s} / \dot{\gamma} = 33.4\text{ 1/s}$ and with the PMMA1-curve at $\eta = 144\text{ Pa} / \dot{\gamma} = 1\,500\text{ 1/s}$.

It is of interest to look at the differences of the ratios of the CS- and the CR-viscosities for the 3 polymers:

for constant shear stress: $\eta_{\text{PMMA3}} / \eta_{\text{PMMA1}} = 6467/144 = 45$

for constant shear rate: $\eta_{\text{PMMA3}} / \eta_{\text{PMMA1}} = 1782/516 = 3.45$

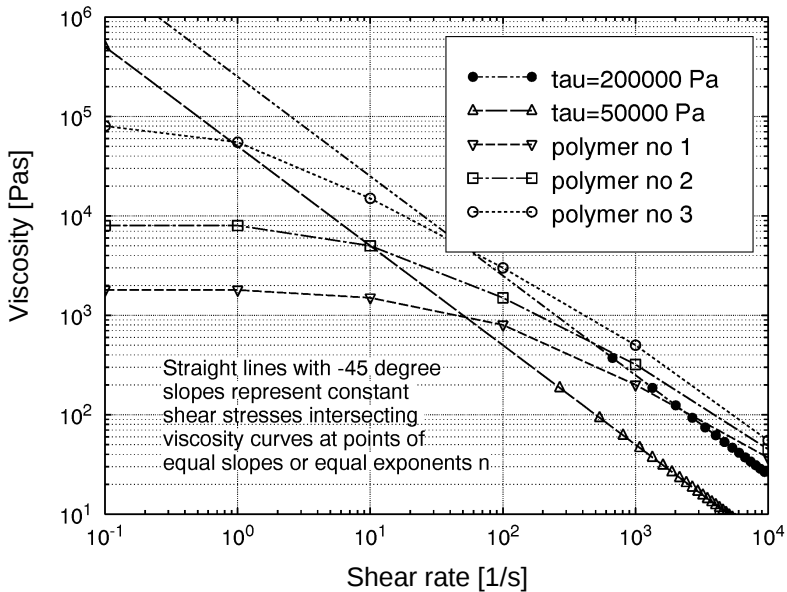


Fig. 23 CS-comparison: viscosity curves of 3 PMMA melts at 220°C

Constant shear stress comparisons have one additional important effect - Fig. 23: All lines of constant shear stress which run parallel at uniform slopes of -45° intersect with the viscosity curves of a polymer family at points of equal slopes, i.e. of equal exponents n . Although the different grades of polymer melts have different viscosity curves a CS-analysis will allow a good comparison since the polymers are equally non-Newtonian and their flow pattern in the capillaries or shearing gaps is alike.

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CR-data comparisons (see Fig. 24) related to a shear rate range 1-10 (1/s) provide different viscosity levels **and** different slopes of the viscosity curves: $n_3/n_2/n_1 = 0.44/0.8/0.92$. This makes a direct comparison of similar polymer melts difficult or even impossible.

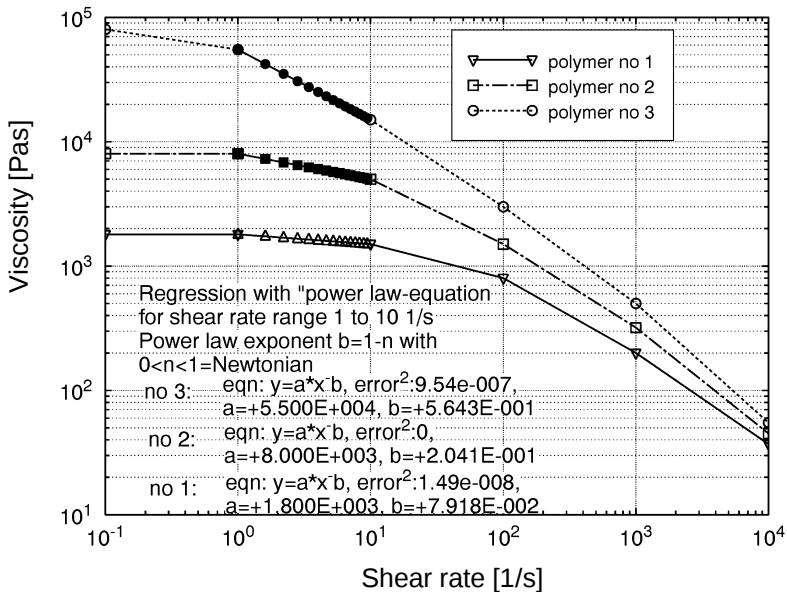


Fig. 24 CR-comparison: Viscosity curves of 3 PMMA melts at 220°C

c.) CS-rheometers out-perform CR-rheometers when testing samples known for their rheological behavior i.e. semi-solids which show solid and viscous behavior as a function of shear rate and shear history.

In chapter 8.2 a detailed discussion of yield point measurements is given. At this point the focus is directed only at the technical differences of both rheometers resulting from their different design principles.

The yield value in this context means that the sample resembles a solid material and volume elements are only elastically deformed for any value of shear stress that does not surpass that critical level named "yield value". Beyond that level the sample flows: the volume elements irreversibly change place with respect to each other. A schematic flow curve of a material characterized by a yield value shows an increase of stress on the ordinate. At the yield value the flow curve suddenly breaks away from the ordinate and keeps climbing with increasing shear rates.

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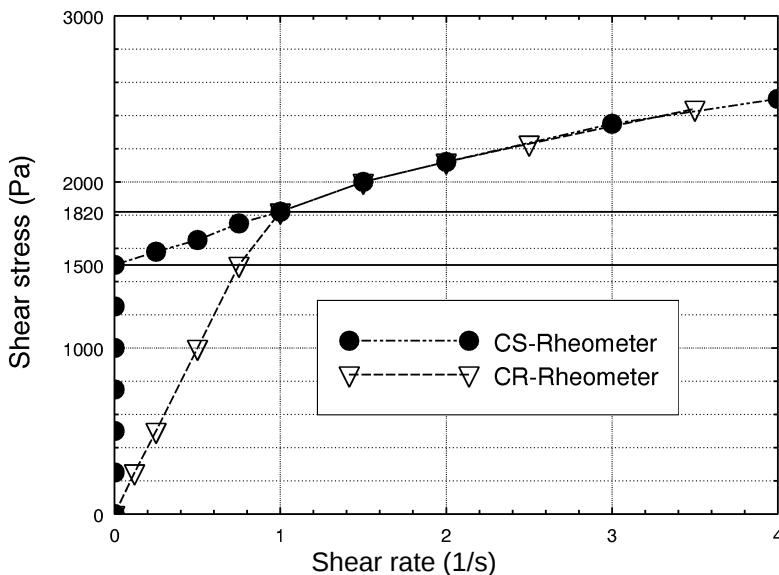


Fig. 25 Comparison of CS- and CR-rheometers for yield point measurements

This is in fact what can be accomplished with a CS-rheometer – Fig 13 – A1: It applies controlled shear stresses but it does not measure any meaningful shear rate as long as stresses are not sufficiently high to overcome the resistance of the sample having a solid nature. The sample “clamps” the rotor at a stand-still. When the yield value is surpassed the rotor starts to rotate and it's deflection is very accurately picked-up by means of an extremely sensitive strain sensor – Fig.25: black dots. Thus the requirements for a true measurement of dispersions which differ in their small yield values are met.

The measuring principle of most CR-rheometers – normally technically less complicated and lower priced than CS-instruments – is different – Fig 13 – B1:

An electrical motor with an attached tachometer-generator is controlled to run at a given rotor speed. The motor rotates the inner cylinder – rotor – of e.g. a coaxial cylinder sensor system, which is encapsulated by the surrounding sample. A torsion detector (soft torque spring: full torque range is accomplished by a 90° deflection) is positioned between rotor and motor. When the rotor rotates in a liquid and thus provides a shear rate, the resistance of the sample against being sheared causes a viscosity-proportional counter-torque or shear stress on the rotor that twists the torsion detector accordingly.

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Testing a sample with a yield value now means that the motor starts to rotate slowly and this speed is determined as an electrical signal by the tachometer-generator. But the rotor encapsulated by the solid-like sample is kept at a stand-still causing only the torque spring to twist. In soft-spring viscometers acting below the yield value the actual speeds of motor and rotor are distinctly different. The flow curve plots a shear stress- and a shear rate increase plotted as a straight line sloping with an angle that deviates clearly from the vertical. The angle of this slope may be correlated to the “spring-factor” of the torque spring. At this beginning of the flow curve the indicated shear rate is not the one of the sample but only a motor and tachometer-generator speed signal – Fig. 25: triangular dots. When the stress within the sheared sample which increases with the motor speed has become so high that the yield value of the sample is surpassed, the rotor actually starts to rotate. It is almost momentarily accelerated from a stand-still to match the speed of the motor. With the beginning of real flow in the sample the flow curve changes its slope almost abruptly and from now on increasing rotational speeds of motor and rotor are identical and can be used to calculate the relevant shear rate. The level of shear stress at the point of sudden change of the flow curve slope is defined as the yield value of the tested sample.

It will be understood that below and around the yield value, CR-rheometers with torque sensors of the soft-spring type give results which do not meet the requirements for a well defined correlation between shear rates and shear stresses. While the uncertainty of the shear rate may only relate to a tiny start phase of the flow curve, it may obscure rheological knowledge of great importance: test results from dynamic tests at small amplitudes or small strains in creep and recovery tests or the ability of small yield values in dispersion prohibiting sedimentation. Even approximations of small yield values are difficult to get with this type of CR-rheometers since they often represent only 4 to 6 % of the total shear stress range, i.e. the yield value may be given with a tolerance range of ± 20 to 30 % – see chapter 6.2.

Please note:

Lately CR-viscometers have become popular equipped with rigid springs as torque detectors which deflect only 0.5° for the whole torque range. Flow curves provided by such a viscometer for fluids characterized by a yield value show only a small angle deviation from the vertical for stresses below the yield value. This angle is again related partly to the spring factor but it is also influenced by some creep deformation of the fluid placed into the sensor system.

CS-rheometers can measure accurately at and around the yield value and their design gives them the potential to determine yield values much more accurately than is possible with the CR-rheometers with spring type stress sensors and a rotor speed measurement by means of the tachometer/generator.

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d.) CS-rheometers are especially designed to determine the visco-elastic properties of fluids and solids, which subjected to small strains in a creep test or to small oscillation amplitudes in a dynamic test, are just elastically deformed but are never forced to flow.

During these tests of the solid phase of samples, the CS-rheometer acts as a sensor “feeling” the “at-rest structure” of this material sample related to the molecular structure or nature of the forces which form a gel structure. Dynamic CS- tests are also very suitable to determine the time-function of chemical or physical changes of samples which cure, harden or gel and which remain mechanically undamaged during these tests.

The CR-rheometers with soft spring torque sensors require surpassing the yield value and they can therefore not cover this area of rheological research on semi-solids.

Summing up this comparison one may conclude, that CS-rheometers have the potential for a much wider and deeper insight into the internal structure of polymers and into important processing characteristics of samples than CR-rheometers/viscometers. The price criteria will however often swing the decision when choosing a new rheometer in favor of CR-viscometers for quality control applications, since they are sold at half or even less the price of modern, versatile CS-rheometers.

The latest computerized models of top-class rheometers having reached the market offer interchangeable CS- and CR-modes. They allow testing yield values accurately in the CS-mode, change automatically at any predetermined threshold value of stress to the CR-mode and then continue to raise the rotor speed to reach high values of shear rate or maintain them for any length of time to guarantee the sol status of thixotropic fluids before reversing the speed program.

Please note:

In literature one often finds that authors have not distinguished between “Searle” and “Couette”. Both types of coaxial cylinder sensor systems for rotational rheometers are then often called “Couette”. In the future one should follow the examples set by the International Society of Rheology, established by German DIN standards etc., thereby differentiating between “Searle” and “Couette” as indicated above.

3.1.3 Equations

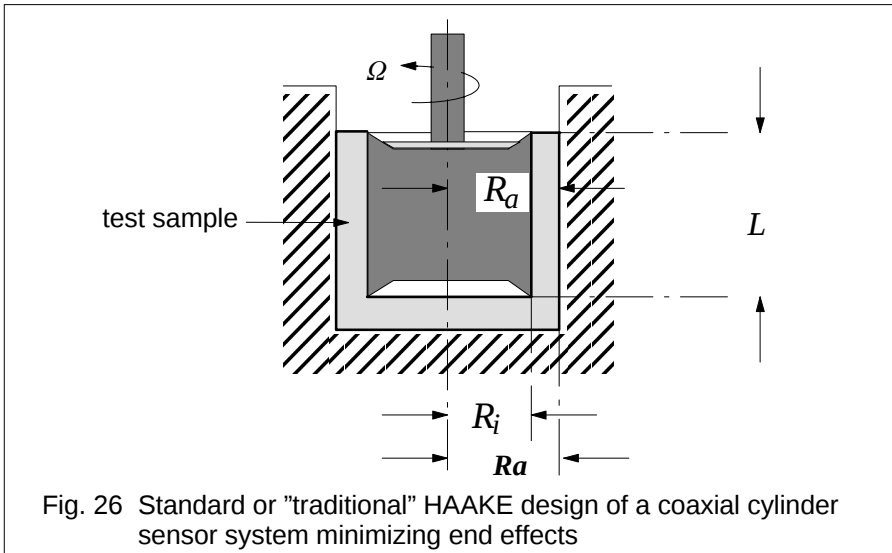
Shear rates and shear stresses are mathematically defined for rotational viscometers/rheometers.

A. Coaxial cylinder sensor systems – German DIN 53018

a) Shear rate at the inner cylinder (rotor)

$$\dot{\gamma}_i = 2 \Omega \frac{R_a^2}{R_a^2 - R_i^2}$$

$$\Omega = \frac{2\pi \cdot n}{60} \quad [11]$$



The shear rate at the rotor surface equals the angular velocity Ω multiplied by a constant "M" which depends on the radii of cup and rotor of a particular sensor system.

It is worthwhile to introduce the ratio of the radii: $\delta = \frac{R_a}{R_i}$ this leads to :

$$\dot{\gamma}_i = \left(\frac{2 \cdot \delta^2}{\delta^2 - 1} \right) \cdot \Omega = M \cdot \Omega = \frac{\pi}{30} \cdot \left(\frac{2 \cdot \delta^2}{\delta^2 - 1} \right) \cdot n \quad [12]$$

$$\dot{\gamma}_r = \frac{R_i^2}{r^2} \cdot \left(\frac{2 \cdot \delta^2}{\delta^2 - 1} \right) \cdot \Omega = \frac{R_i^2}{r^2} \cdot M \cdot \Omega \quad [13]$$

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- $\dot{\gamma}_i$ = shear rate at rotor radius R_i [s^{-1}]
- $\dot{\gamma}_r$ = shear rate at radial coordinate r [s^{-1}] within the gap $R_a - R_i$
- δ = ratio of radii
- Ω = angular velocity [rad/s]
- R_a = radius of the cup [m]
- R_i = radius of the rotor [m]
- n = rotor speed [min^{-1}]
- M = shear rate factor or geometry factor [$s^{-1}/rad \cdot s^{-1} = 1/rad$] - it combines all factors given in the above bracket (), i.e. it depends on the radii of the cup and the rotor.

b) Shear stress τ

$$\tau_i = \frac{M_d}{2\pi \cdot L \cdot R_i^2 \cdot Cl} = \left(\frac{1}{2\pi \cdot L \cdot R_i^2 \cdot Cl} \right) \cdot M_d^{[14]}$$

$$\tau_i = A \cdot M_d$$

$$\tau_a = \frac{M_d}{2\pi \cdot L \cdot R_a^2 \cdot Cl}$$

$$\tau_r = \frac{M_d}{2\pi \cdot L \cdot r^2 \cdot Cl} \quad [15]$$

- τ_i = shear stress at the radius R_i [Pa]
- τ_a = shear stress at the radius R_a [Pa]
- τ_r = shear stress at the radial coordinate r [Pa]
- M_d = torque to be measured [$N \cdot m$]
- L = rotor height [m]
- A = shape factor [m^{-3}] - it combines all factors in the above bracket (). It is a constant for the particular sensor system defining the geometry of the rotor.
- Cl = torque correction factor which incorporates rotor end face effects. The evaluation requires the knowledge of τ_i and τ_r , while τ_a is for most tests less important.

c) Deformation gamma γ

The deformation gamma is linearly linked to the angular deflection φ and the rotor dimensions:

$$\gamma = M \cdot \varphi \text{ with } \varphi = \text{angular deflection [rad]} \quad [16]$$

d) Viscosity η

$$\eta = \frac{M_d}{\Omega} \cdot \frac{A}{M} = \frac{M_d}{\Omega} \cdot G [Pa \cdot s] \quad [17]$$

With $G = \frac{A}{M}$

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B. Cone-and-plate sensor systems

a. Shear rate $\dot{\gamma}_c$

$$\dot{\gamma}_c = \frac{1}{\tan \alpha} \cdot \Omega = M \cdot \Omega \text{ [s}^{-1}\text{]}$$

$$M = \frac{1}{\tan \alpha} \approx \frac{1}{\alpha} \quad \Omega = \frac{2\pi \cdot n}{60} \quad [18]$$

Ω = angular velocity [rad/s]

n = rotor speed [min⁻¹]

α = cone angle [rad]

M = shear rate factor [1/rad]- as given above. It is a constant for the particular cone-and-plate sensor system.

Cone angles in commercial cone-and-plate sensor systems are normally very small ($\alpha = 0.0174$ rad (1°)). Smaller cone angles are sometimes offered but for them the correct gap setting is very critical and they are therefore less recommended. It is therefore acceptable to approximate in the above equation: $\tan \alpha \approx \alpha$. Cone angles up to $\alpha = 0.698$ rad (4°) are often used for dispersions with larger sized fillers.

Cone angles α are chosen in such a way that for any point of the cone surface the ratio of angular speed and distance to the plate is constant, i.e. the shear rate $\dot{\gamma}$ is constant from the cone tip to the outer radius R_c .

Constant $\dot{\gamma}$ can also be assumed for any point within the gap. Setting the cone so that it's tip just touches the plate is very critical especially when using cones with small cone angles. As an example: setting a cone with $R_c=17.5$ mm and a cone angle of 1 degree only 15 microns too high this will cause a 5 % error in the viscosity measurement!

R_c = Outer radius of cone
 α = Cone angle
 R_T = Truncation radius
 a = Height of removed tip

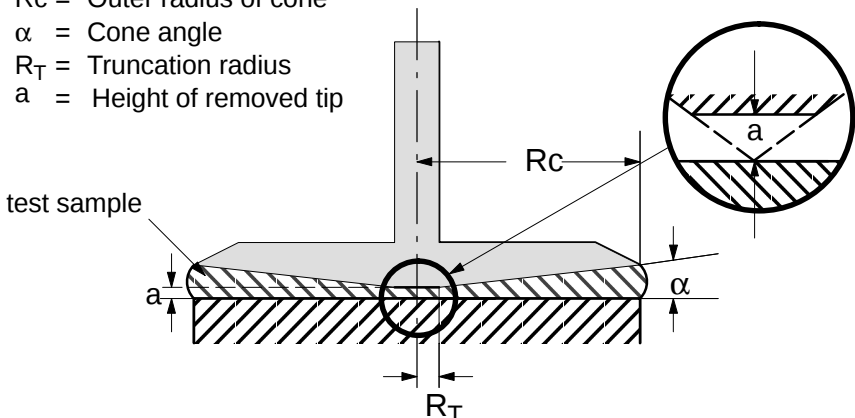


Fig. 27 Cone-and-plate sensor system with truncated cone

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To avoid that the cone tip and the center of the plate wear too much when testing dispersions with abrasive fillers resulting in a falsified positioning of the cone versus the lower plate, it is common to use “truncated” cones: the tip of the cone is ground off up to a truncation radius R_T – Fig. 27. This also means that the axial height of the cone is reduced by the value a . When preparing the cone-and-plate sensor system for a test, the cone is first moved downwards until the truncated cone contacts the plate. The cone is then moved upwards by the axial distance a . When now the test is run the imaginary tip of the cone is just touching the plate as is required for the cone-and-plate tests. The error involved on the measured torque or shear stress due to the removal of the tip is related to the ratio of the cone surface area to the area of the truncation. For a cone with $R_c=30$ mm and $R_T=3$ mm, the truncation error is 1%. The effect of truncation becomes more important for cones of smaller R_c . Truncation may be considered as a compromise between the wish for optimum test results and the minimization of errors that might occur unnoticed due to wear on the cone-and-plate sensor systems.

b. Shear stress

$$\tau_c = \left(\frac{3}{2\pi \cdot R_c^3} \right) \cdot M_d = A \cdot M_d \quad [19]$$

τ_c = shear stress on the cone [Pa]

R_c = outer radius of the cone [m]

M_d = torque to be measured [N·m]

A = shear stress factor as contained in the above bracket – it is constant for a given cone-and-plate sensor system.

c. Viscosity η

Viscosity is determined making use of the equation as used for the coaxial cylinder sensor system:

$$\eta = \frac{M_d}{\Omega} \cdot \frac{A}{M} = [Pa \cdot s] \quad [20]$$

Often the coefficients A and M required for the evaluation of shear rate and shear stress for a particular sensor system are combined:

$$G = A / M$$

G = geometry factor for a sensor system

C. Parallel-plate sensor systems

It is determined by the plate radius R and the distance h between the plates – Fig.28. This distance can be varied. It should be not smaller than 0.3 mm and

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not larger than 3 mm since otherwise sizeable measuring errors related to the nature of the sample cannot be avoided. Parallel-plate sensor systems are chosen instead of cone-and-plate sensor systems if samples containing larger filler particles are to be measured rheologically. The chosen gap size should be at least 3 times larger than the biggest particle size.

a.) Shear rate

Please note:

The shear rate of this sensor system is dependent on the specific radius r of the plates: $0 < r < R$. The shear rate given for such a sensor system is calculated for the outer radius R . For the viscosity measurement of Newtonian liquids it does not matter that this sensor system is not characterized by a single shear rate but by a wide shear rate range from zero at the plate center and high at R . For non-Newtonian fluids the shear stress must be corrected.

$$\dot{\gamma}_{\max} = M \cdot \Omega \quad [1/s]$$

M = geometry factor = R/h with R = outer plate radius [m]

h = gap size between plates [m]

$$\Omega = \frac{2\pi \cdot n}{60} \quad \text{whereby } n = \text{rotor speed } [min^{-1}]$$

b.) Deformation γ :

It relates the geometry of the sensor system with the angular deflection

$$\gamma = M \cdot \varphi \quad \text{with } \varphi = \text{deflection angle } [rad]$$

c.) Shear stress τ :

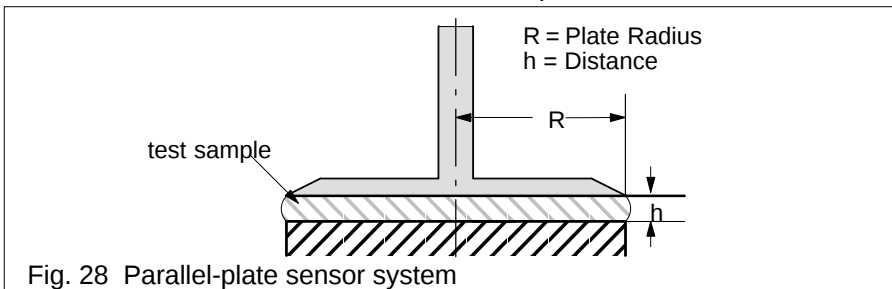
The shear stress at the outer edge of the plate is proportional to the torque M_d and the geometry factor A .

$$\tau = M_d \cdot A \quad [Pa]$$

$$A = \frac{2}{\pi \cdot R^3} \quad \text{with } R = \text{outer plate radius } [m]$$

For fluids that show a non-Newtonian flow behavior (power-law-exponent $n < 1$) the shear stress must be corrected according to Weissenberg:

$$\tau = M_d \cdot A \cdot \left(\frac{3 + n}{4} \right) \quad [21]$$



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The constants A and M follow HAAKE nomenclature. Other viscometer manufacturers or text books may use different letters to describe the same constants.

3.1.4 Quality criteria

Rheological quality depends on the following criteria:

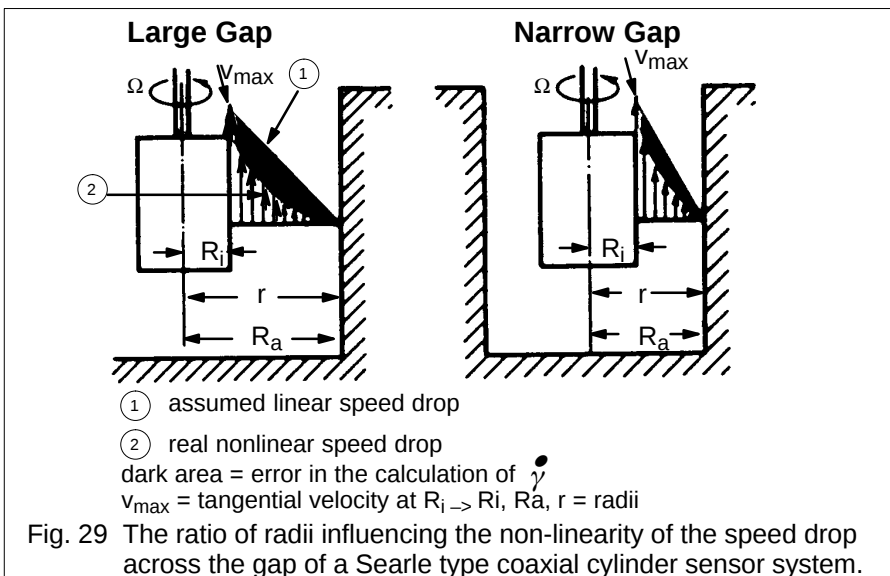
A. Coaxial cylinder sensor systems

a. Ratio of the radii

The equation for shear rate [4] was approximated by the simple equation [5]

$$\dot{\gamma} = \frac{v_{\max}}{y} [s^{-1}] = \frac{v_{\max}}{R_a - R_i} \quad [22]$$

This was true for the parallel plate model and Newtonian liquids. When turning the plates into cup and rotor, the velocity gradient across the gap $y = R_a - R_i$ becomes non-linear. It is easy to determine the maximum speed v as the tangential speed of the rotor. If one simply divides $v_{\max}$ by y to calculate not only the relevant shear rate for conditions near the rotor surface but for any point between R_a and R_i , then a sizable error will be introduced. This error is indicated in Fig. 29 by the two shaded areas between the assumed linear and the real non-linear velocity gradient across the gap size. This gradient will become even more non-linear when non-Newtonian liquids instead of Newtonian are tested.



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This error can be minimized by reducing the gap size, which linearizes the velocity gradient across $R_a - R_i$. Instead of using the difference of the radii to define the annular gap size, it is common to use the ratio of the radii [12]:

$$\delta = \frac{R_a}{R_i}$$

This ratio in a real sensor system of a rotational rheometer will always be bigger than 1.00. A ratio of 1.00 would only be possible when both radii are identical and the gap has shrunk to zero. The closer this ratio comes to 1.00, the better it is rheologically. In the following example a ratio of 1.10 already leads for the same rotor speed n to a shear rate 12 % less than that of $R_a/R_i = 1.01$ and the corresponding viscosity values differ by 37%. Inasmuch as the ratio of the radii is of such an importance for the accuracy of the measurement of the viscosity of non-Newtonian fluids, the German DIN and international standards have set this limit:

$$1.00 \leq \delta \leq 1.10$$

Sensor systems with only a rotor and without a cup, i.e. the rotor hung into a large liquid container, have very big or undefined values of R_a . Their ratio δ approaches "infinity" which is the worst possible value.

$$\delta_1 = 1.01 \rightarrow \dot{\gamma}_1 = \frac{\pi}{30} \cdot \frac{2.0201}{0.0201} \cdot n \approx 10.60 \cdot n$$

$$\delta_2 = 1.10 \rightarrow \dot{\gamma}_2 = \frac{\pi}{30} \cdot \frac{2.21}{0.21} \cdot n \approx 1.10 \cdot n$$

$$\delta_3 = \infty \rightarrow \dot{\gamma}_3 = \frac{\pi}{30} \cdot \frac{\infty}{\infty} \cdot n \approx 0.105 \cdot n$$

Example: Fig. 30 indicating the influence of gap sizes on viscosity data when non-Newtonian liquids are tested.

$$\begin{aligned} \text{for } n = 10 \text{ rpm} \quad \dot{\gamma}_1 &= 106.0 \text{ 1/s} \Rightarrow \eta_1 = 6.78 \text{ mPas} \\ \dot{\gamma}_2 &= 11.60 \text{ 1/s} \Rightarrow \eta_2 = 10.72 \text{ mPas} \\ \dot{\gamma}_3 &= 1.05 \text{ 1/s} \Rightarrow \eta_3 = 19 \text{ mPas} \end{aligned}$$

Please note: If a Newtonian liquid is tested different gap sizes or different values of δ of sensor systems or even just a rotor in a wide open container will not influence the viscosity data of such a measured sample.

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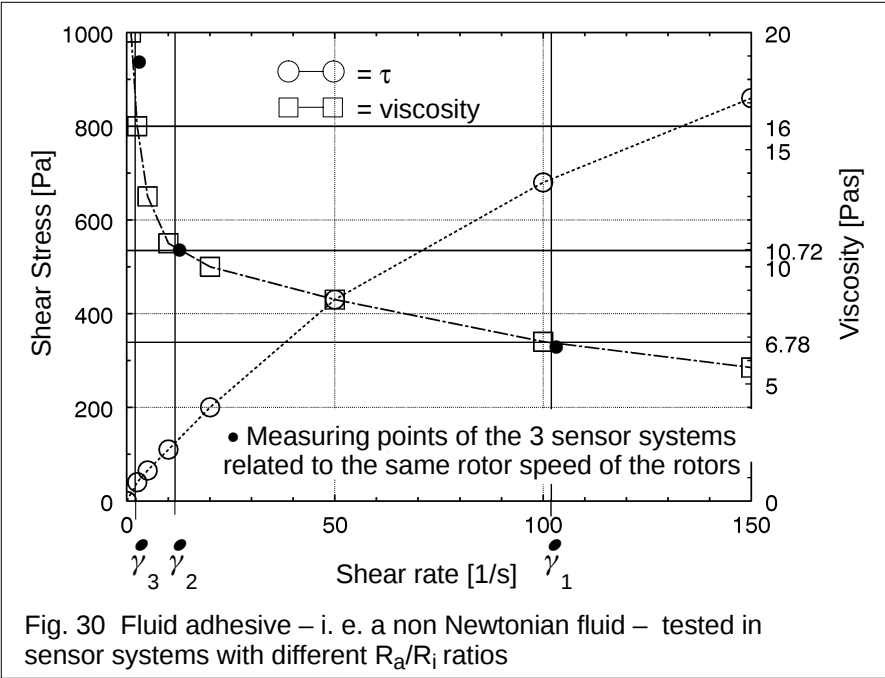


Fig. 30 Fluid adhesive – i. e. a non Newtonian fluid – tested in sensor systems with different R_a/R_i ratios

Test results are shown in Fig. 30 to indicate the magnitude of the deviations in shear rate and viscosity with the change of R_a/R_i . The viscosity curve of a fluid adhesive being highly non-Newtonian is used to demonstrate graphically how, for a common rotor speed of 10 rpm, the change in shear rate from $\dot{\gamma}_1 = 102 \text{ 1/s}$ for $\delta_1 = 1.01$ to $\dot{\gamma}_3 = 2 \text{ 1/s}$ for a $\delta = \infty$ results in a viscosity value that increases to 280%. This is the result of the measurement at very different shear rates and the pseudoplasticity of the sample.

This is a clear indication of the fact that measuring viscosities of non-Newtonian liquids can lead to very wrong results when just a rotor of the viscometer is hung in a container as large as “the North Atlantic”. Rheologically it would be acceptable if this measuring set-up were used for Newtonian liquids (the viscosity of which is independent of shear rate), but one has still to be aware of the risk that in very large open containers it may be difficult to guarantee a uniform temperature. When choosing a rheometer/viscometer with coaxial cylinder sensor systems for a particular liquid one must carefully select sensor systems with the smallest possible ratio of R_a/R_i keeping in mind that disturbing problems may occur with filler particles larger than 1/3 of the gap size. For an accurate absolute viscosity measurement of non-Newtonian liquids, the selection of small values δ is the most important quality criteria.

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b. "End effects" related to the rotor end faces

The mathematical treatment of viscometer data requires that the torque to be measured must be solely created by the resistance of the liquid sample being sheared in the well-defined shearing gaps as e.g. in the annular gap of coaxial cylinder sensor systems. However all inner cylinders/rotors have bottom and top end faces and an additional torque may arise from shear between these end faces and the outer cylinder/cup. This will constitute a torque error which is an unknown part of the total value Md measured by the torque sensor.

Selecting suitable geometries for coaxial cylinder sensor systems will minimize these end face effects:

(1) Very small gap size $\delta \cong 1.01$ – Example of a sensor system: "high shear HS1" with a $\delta = 1.003$ which for high values of n provides high $\dot{\gamma}$.

If the gap size is made very small and the distance of the rotor end face to the bottom of the cup is about 100 times bigger, the end effect becomes negligible.

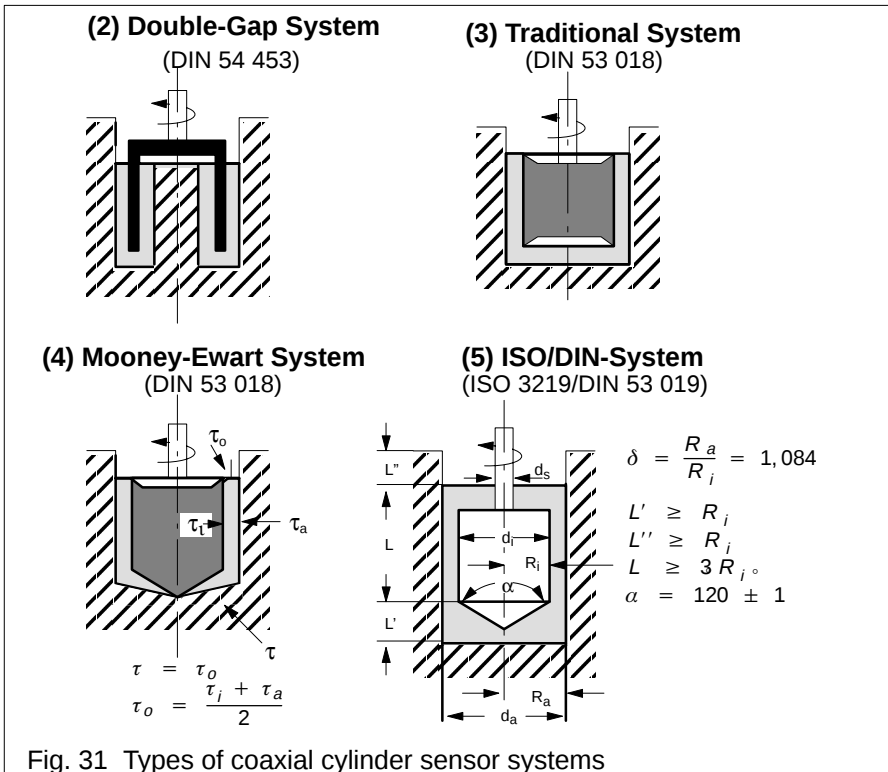


Fig. 31 Types of coaxial cylinder sensor systems

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(2) Double gap sensor systems

The rotor is bell-shaped. The sample contacts the rotor on the inside and on the outside. Both end faces are thin circular rings causing almost no end effects.

Conditions in the outer gap are “Searle” and in the inner gap “Couette”

(3) “Traditional” HAAKE design of rotors and cups – German DIN 53018

Bottom and top end faces of the rotor are recessed.

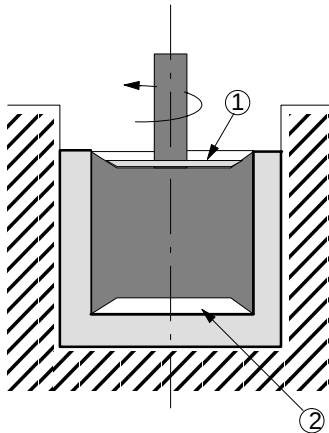


Fig. 32 Rotor design “standard” with recessed top and bottom end faces eliminates end effects.

- In the bottom recess (2) air is entrapped when the rotor and the cup filled with the sample are brought together. The entrapped air bubble covers some 90% or more of the bottom endface. When the rotor rotates, the air cushion at the bottom surface prevents the sample from being sheared underneath the rotor and eliminates the normal torque contribution of the rotor bottom endface. Only the small rim around the recess adds a tiny torque which is taken care of in the evaluation of the “A”-constant.
- The recess at the top of the rotor (1) allows any surplus of the sample to spill over into that cavity so that again the rotor - when rotating - shears only air with its top end face and thus here too an “error torque contribution” is prevented.

This type of sensor system is not to be used if tests require programmed changes of the test temperature covering a wide temperature range inasmuch

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as the air enclosed in the lower recess will expand or shrink more than the test liquid. Thus either heated air will bubble into the sample in the shearing gap causing test value variations or test liquid will be drawn into the lower recess if the cooled air volume has shrunk and this will increase the end effect on the measured viscosity data.

(4) Mooney-Ewart design

It allows the calculation of the bottom end face effect by creating a flow in a double cone gap. The design requires such an angle between the rotor and the cup cones so that the mean shear stress τ_0 in the conical bottom gap equals the mean shear stress τ between the two cylindrical surfaces. This design allows every volume element to contribute to the torque measurement, i.e. best use is made of the sample available. This will be very important if only a few milliliters of a sample are available as i.e. in the case of the viscosity testing of whole blood of infants. In comparison: Standard sensor systems require quite a lot of “dead volume” below the rotor to keep the error contribution small. Depending on the particular design features, the double cone gap in a Mooney-Ewart sensor system may contribute some 20% to the total measured torque.

(5) ISO and DIN-type cup and rotor design – ISO 3219 and DIN 53019

It standardizes ratios of radii, of rotor length versus rotor radius and of the distance between the tipped rotor bottom versus the bottom of the cup. Standardizing these ratios will mean that the percentage of errors due to the non-linearity of the shear rate across the gap and to end effects are kept constant for small and big coaxial cylinder sensors. ISO/DIN-type sensor systems are the result of a reasonable compromise between rheological requirements and the anticipated applicability for a wide spectrum of liquid samples. These sensor systems decrease differences in test results which cause concern when testing one type of sample in various rotational viscometer models manufactured on the world market. These differences often have to be related to the different design features used by the viscometer manufacturers concerned.

The ratio $\delta = 1.0847$ of the ISO/DIN-sensor system is near to the upper limit of δ mentioned. Whenever possible – for instance when testing liquids with no or only very small particles – sensor systems such as described in A, B, C and D with values of δ nearer to 1.00 should be preferred to the ISO/DIN-type sensor systems.

Please note:

Sensor systems with just a disk-type rotor in an undefined container, are not acceptable for absolute viscometry. Their torque originates up to 90% from their upper and lower end faces and the shear rate function in the sample container cannot be calculated.

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B. Cone-and-plate sensor systems

The quality of the test results is best with small cone angles α . Cone and plate sensor systems have preferably a cone angle α of 0.0174 rad (1°). The following point should also be considered: Large errors of measurement data are encountered if the contact between the cone and the plate is neither well set nor maintained and a reasonable control of the sample temperature is lost when the sample is subjected to high shear.

3.1.5 Comparison of coaxial cylinder- and of cone-and-plate-sensor systems

Both types of sensor systems give in theory identical test results for homogeneous Newtonian and non-Newtonian liquids. Still there are some differences in the applications of these sensor systems worth noting:

Generally, one cannot go wrong choosing coaxial cylinder sensor systems. There are sensor systems particularly suitable for low shear and for high shear testing at low or high test temperatures and for low or high viscosities. The jacketed outer cylinder which fully surrounds the inner cylinder allows a good temperature control for the sample tested. The annular gap is of constant width: tests may be run with samples that contain particles with a particle size less than 1/3 of the gap size. While some sensor systems – especially those of the Mooney-Ewart design – require sample volumes of only a few cm^3 , all other coaxial cylinder sensor systems need sample volumes of 5 to 50 cm^3 .

Cone-and-plate (PK) sensor systems

“Cone-and-plates” are often chosen when cleaning at the end of a test is a problem. For very many quality control tests per day on highly pigmented dispersions, the cleaning of the cup and the rotor of a coaxial cylinder sensor system is so much more troublesome and time-consuming than the cleaning of the “easy to get at” cone-and-plate. For “resistor pastes” containing precious metals it is important that almost all of the valuable sample can be recovered by simply scraping it off the cone and the plate.

An important argument for choosing a “cone-and-plate” is often that the sample size available is normally much smaller than the sample size required for most cup-and-rotor sensor systems. This will matter in cases that the sample is very precious or only a few drops of a sample exist. The list below indicates some typical volumes for common “cone-and-plates”: often a few drops of liquid will suffice. Sample volumes differ with the chosen cone angle and radius. Typical are: angles: $\rightarrow 0.5^\circ$, 1.0° and 4.0° ; radii: $\rightarrow 10$, 17.5 and 30 mm

HAAKE sensor systems	C20/1	C35/1	C60/1	C60/4
diameter (mm)	10	17.5	30	30
cone angle ($^\circ$)	1	1	1	4
volume (cm^3)	0.02	0.2	1	4

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Cone-and-plate sensor systems have their main application in the high shear rate range up to $\dot{\gamma} = 10^4 \text{ s}^{-1}$. Limitations as to maximum shear rate are set less by the geometry of this type of sensor system than by the “Weissenberg effect”, by shear heating and by secondary flow.

The time/temperature related viscosity increase that occurs as a result of chemical reactions such as hardening or curing can be measured and recorded. If the polymer has changed during this chemical reaction into a hard solid mass, it is important that the cone can be separated from the lower plate easily to allow the removal of the cured polymer specimens. Coaxial cylinder sensor systems for obvious reasons cannot be used for the testing of the cure of thermosetting resins.

Limitations for the use of the cone-and-plate sensor systems:

The conical rotor means that the gap size between the cone and the plate varies from being zero at the cone tip to a maximum at the cone radius R_c . Dispersions with particles of even the smallest size are obviously still too big for the gap size near the cone tip. When the “cone-and-plate” is used for dispersions with sizable particles such as pigments in printing inks or paints with large filler aggregates these particles must be squeezed from the tip region outwards to allow cone contact. This radial flow in the phase of filling the measuring gap properly requires quite some axial force especially in the case of samples having a strong yield value resisting this radial squeeze flow. On thixotropic dispersions such as creams or ointments the radial squeeze flow will mean some pre-shear and a partial destruction of the thixotropic structure. During a test of inks or paints a secondary flow of particles in a radial direction may be created and superimposed on the main circular flow negatively affecting the otherwise predominant laminar flow. This also causes heterogeneous samples with a high filler content to become even more non-homogeneous during a test. Particles of bigger size require the use of cones having a larger than standard angle: up to 0.0532 rad (1° or even 4°) which will increase the negative effects of secondary flow on the test results.

Cone-and-plate sensor systems are more than coaxial sensor systems affected by normal forces which are the result of elastic responses of visco-elastic samples when they are subjected to shear. These normal forces are able to draw volume elements of the tested sample out of the angular gap and make them climb upwards on the outer rim of the cone. When the sample is partly sucked out of the gap it causes a partial split of the sample in the middle of the angular gap (see Fig. 33 ②). This is a serious disturbance for the viscosity measurement. A ridge of the sample which appears at the rim of the cone and becomes bigger for higher shear rates is an indication of this disturbance. One can often see the actual split within the angular gap when visually looking closely at the rotating cone.

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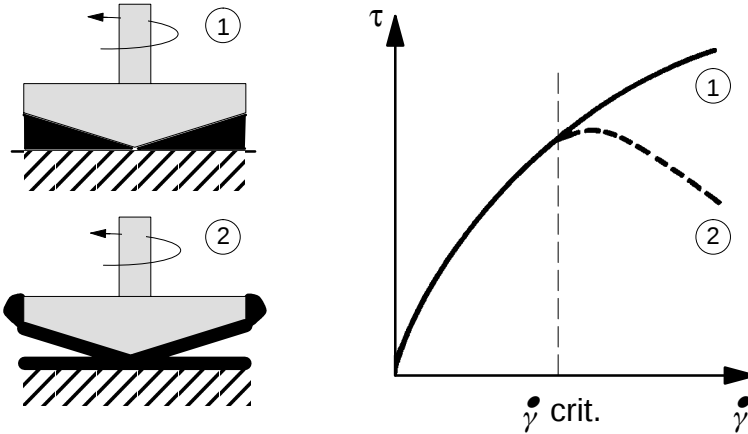


Fig. 33 Testing viscous and visco-elastic samples in a cone-and-plate sensor system

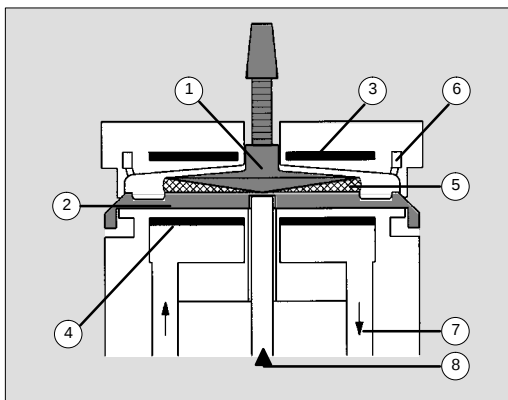
The disturbance caused by the normal forces can also be detected in the flow curve (see Fig. 33 – right side). The continuous line ① describes the flow behavior of a purely viscous liquid. The dashed line ② indicates that the curve of the visco-elastic liquid breaks away from the true curve ① when above a critical shear rate the split of the sample within the angular gap has become sufficiently large. It is obvious that it would not make sense to evaluate any test results having been measured at shear rates above the critical level.

The special sensitivity of a cone-and-plate-sensor system to normal forces generated by visco-elastic samples reduces the use of this sensor system very often to low shear rates for samples for which the theoretical potential of a “cone-and-plate” to reach high shear rates appeared so advantageous.

The normal force which is proportional to the elastic property of a fluid may be measured by means of a suitable pressure sensors that may be installed in the lower plate. It measure the force that acts to part the cone from the lower plate.

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- | | | | |
|---|-------------------------|---|-------------------------------------|
| 1 | Cone with ceramic shaft | 5 | Test substance in the measuring gap |
| 2 | Lower plate | 6 | Ring gap for inert gas |
| 3 | Upper heater | 7 | Compressed air cooling path |
| 4 | Lower heater | 8 | Temperature sensor |

Fig. 34 High temperature sensor system for a rotational rheometer
– HAAKE RheoStress RS100 –

Accurate measurements always require a good temperature control. At preset temperatures well above ambient it is essential that only special cone-and-plate sensor systems are used, which provide an accurate temperature control for **both** the plate and the rotating cone. Additionally it is advantageous if heat losses along the rotor shaft into the rheometer are minimized by e.g. a ceramic intermediate shaft element. An example of a design of such a cone-and-plate sensor system suitable for testing melts at high temperatures is illustrated in Fig. 34. Both the cone – by radiation from the heater plate above – and the lower plate are electrically heated to the required test temperature.

But even the best thermal control of the sensor system cannot totally avoid that when testing samples of high viscosity at constant high shear, more frictional heat is developed inside of the sheared sample than can be removed in the same time interval by heat conduction into the surrounding cone and plate. The sample volume filling these sensor systems being small and the torque being high causes the mass temperature to rise beyond reasonable limits making the test results less significant. Good cone-and-plate sensor systems have temperature sensors installed which can monitor the amount of shear heating and can initiate the termination of such a test when the temperature rise has become too high. "Too high" can be already a $\Delta T = 1^\circ\text{C}$.

Testing samples containing abrasive particles will cause wear especially on the cone tip and on the center of the plate. This will change the dimensions of

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the very small angular gap and negatively influence the test results. The problem of wear is more serious on the cone-and-plate- than on comparable coaxial sensor systems.

It is safe to assume that a cone-and-plate sensor system subjected to some or all of the above influences will give a lower accuracy (not better than $\pm 3\%$) measuring the viscosity of a sample than comparable coaxial sensor systems (not better than $\pm 2\%$)

Rheometers are designed to allow an easy exchange of both a multitude of cone-and-plate- and coaxial cylinder sensor systems characterized by their different active surface areas. It is technically simpler to design coaxial sensor systems of much larger surface area for the testing of low viscosity liquids than it is possible for a “cone-and-plate”.

This leads to the conclusion that cone-and-plate sensor systems are less suitable for the measurement of low but more for medium and high viscosity samples.

Parallel-plate sensor systems are to quite an extent an alternative to a cone-and-plate sensor system.

They require a higher sample volume than the cone-and-plate sensor system of equal cone radius, but this volume is still only a small fraction of what is normal in coaxial cylinder sensor systems. They are able to avoid problems with samples containing large filler aggregates. They may be used when tests should be run at relatively low shear rates. These sensor systems facilitate filling the shearing gap with samples having strong yield values inasmuch as they do not require a significant radial squeeze flow to reach the final gap size between the plates prior to the actual test.

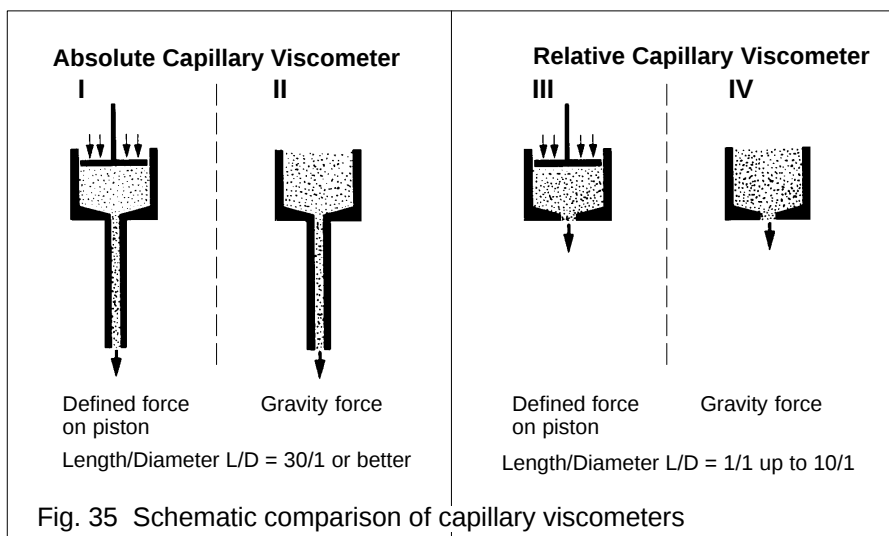
Parallel-plate sensor systems when used to determine the shear rate dependency of the viscosity of liquids showing a distinct non-Newtonian flow behavior require the Weissenberg correction to take care of the variation of shear rate as a function of the plate radius – see also paragraph 9.5.3.

Parallel-plate sensor systems are very common for the testing of a multitude of samples for their visco-elastic properties by means of modern CS-rheometers. While “cone-and-plates” with small cone angle are very suitable for the viscosity measurement of non-Newtonian liquids the parallel-plate sensor systems with wide gap sizes of some 2 mm may rather be used for the elasticity measurement of semi-solids and visco-elastic fluids exhibiting for instance high yield values.

3.2 Capillary viscometers

3.2.1 Indication of different models – Fig. 35

Quite a number of simple and sophisticated instruments fall in this group of viscometers which are designed to measure viscosity but not elastic properties even if the samples are visco-elastic.



Well designed capillary viscometers allow a liquid to flow as indicated in Fig. 2c. Capillaries can have round or slit cross-sections. Laminar flow in capillaries can be understood as a sliding of nested tube-like layers telescopically over each other.

With respect to the design of capillary viscometers and the quality of their viscosity test results, one differentiates between those which provide variable pressure to force liquid through the capillary or those that use gravity as the driving force. In addition capillaries may have either long or short capillaries or high or low ratios of capillary length L to capillary diameter D .

Testing can be done in the CS-mode with a pressure provided and the resulting flow rate being measured or in the CR-mode, for which a controlled flow rate is preset by means i.e. of a melt pump and the resulting pressure drop along the length of the capillary is determined.

3.2.2 Variable pressure capillary viscometers

A. Capillary Rheometer Slit Die (Model I in Fig.35)

A plunger, extruder, or other pressure source drives the sample through a slit capillary at either constant or programmed flow rates.

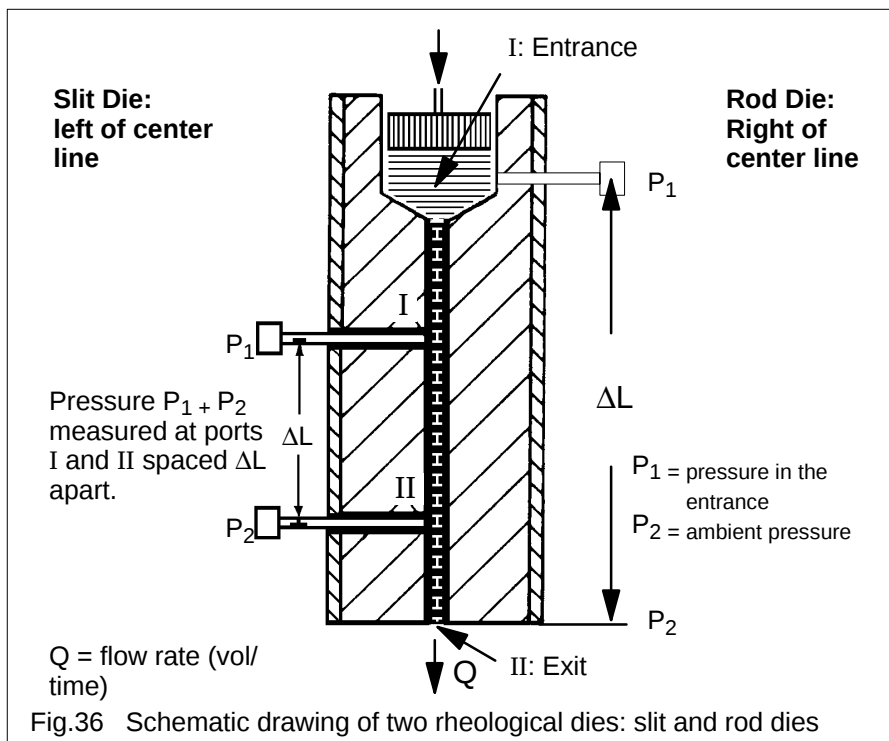
The resistance of the sample to flow through this capillary causes a pressure drop between the two points I and II (Fig. 36). The pressure ports are spaced apart by a capillary length ΔL and they are normally situated sufficiently far away from both the entrance to and exit from the capillary to limit or even eliminate entrance and exit errors caused by elasticity related effects of the melts and by non-laminar flow. Two pressure transducers mounted flush with the slit surface measure the pressure drop $\Delta P = P_1 - P_2$. Pressure sensors/transducers have a thin metal diaphragm, which is bent by the melt pressure. The mechanical deflection of the diaphragm is converted into a proportional electrical signal. Pressure sensors designed to stand up to high pressures have relatively thick diaphragms which provide an unsatisfactory resolution for the measurement of low pressure values.

The forward movement of the plunger with time or the drive speed of a metering pump defines the flow rate Q (cm^3/min). Alternatively one can weigh the extrudate for a given time span and transform the weight signal with the known density of the mass into a value of mass flow rate. The viscosity of the samples tested is linked to the pressure drop within the capillary and to the flow rate.

This design of a slit die with its' pressure ports allows the sample flowing through the capillary to reach a steady state and laminar flow to occur before arriving at point P_1 , i.e. any influence of entrance effects on the pressure difference is avoided. At the points I and II the kinetic energy in the extruded mass is identical, so that kinetic energy related to exit effects does not affect the pressure difference within the capillary length ΔL . Under these conditions and for liquids showing a Newtonian flow behavior, both the shear stresses and the shear rates can be exactly calculated.

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Application of capillary extrusion

Capillary rheometry has found its main area of application in the measurement of polymer melt viscosities at medium and high shear rates and at temperatures that reach up to 500°C. When using slit capillaries one can measure the pressure difference directly in the capillary as shown in Fig. 36 (left side) but this limits the shear rate range to values rarely exceeding $\dot{\gamma}=1000$ 1/s. Higher shear rates up to $\dot{\gamma}=10\,000$ 1/s require the use of rod capillary dies with die diameters varying between approx. 1 to 3 mm. In rod capillary rheometry the relevant pressure difference cannot be determined inside the capillary but the evaluation uses the difference between the pressure measured in the reservoir leading into the capillary and the ambient pressure at the die exit. There are no pressure sensors small enough to be installed into small rod capillaries. The measured pressure difference in rod capillary rheometry is greatly affected by so called entrance errors caused by elastically stored energy in the highly sheared melt, non-laminar flow in the entrance region and non-steady-state flow conditions when the melt is accelerated to flow through a capillary with a small diameter.

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To minimize the relative magnitude of the entrance effects on the measured pressure difference, capillaries are used with a high ratio of capillary length L to radius R ($L/D=20/1$) or even higher.

The use of piston-type capillary rheometry has been limited lately to simpler “melt indexers”. Most modern capillary rheometers for the testing of polymer melts use laboratory extruders to melt and homogenize the polymers continuously and they provide a high enough pressure to force the melt through capillaries of small radius and long length. Often it is advantageous to place melt-pumps between the extruder and the capillary rheometer dies to stabilize the flow through those capillaries at high pressures.

In capillary rheometry the “rheometer” as such is the “rheometer-die” itself with the means to measure the pressure difference ΔP proportional to the shear stress and the flow rate Q proportional to the shear rate. This flow rate Q can be determined for melts of known gravity at the test temperature by weighing the extrudate per time unit on a computerized balance.

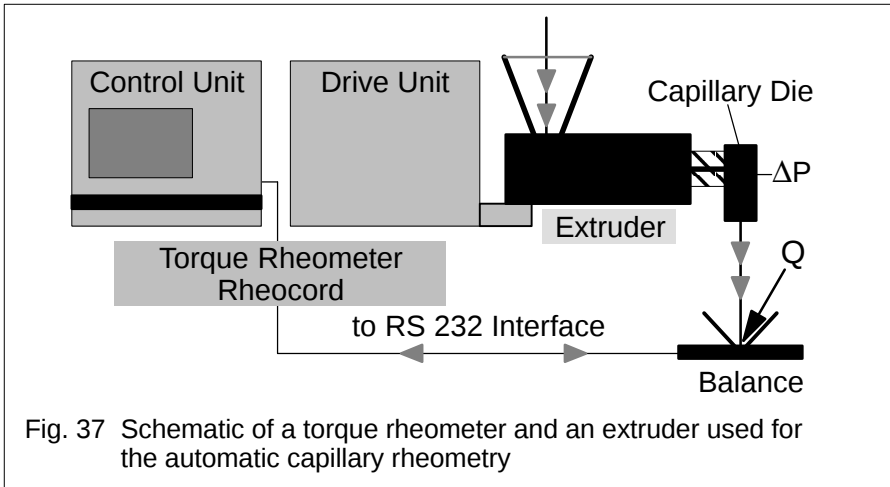


Fig. 37 Schematic of a torque rheometer and an extruder used for the automatic capillary rheometry

High shear rate testing means that a lot of energy causing the sample to flow is transformed into heat. This leads in rotational rheometers as described before to a remarkable rise in the sample temperature well above the preset temperature level and consequently to errors in the viscosity measurements if the temperature rise is not accounted for. It is one advantage of capillary rheometers in comparison to rotational rheometers that most of the heat caused by high shear testing is removed continuously from the capillary by the extruded sample and therefore this shear heat does not accumulate in the rheometer. Still the shear induced temperature rise remains a grave problem.

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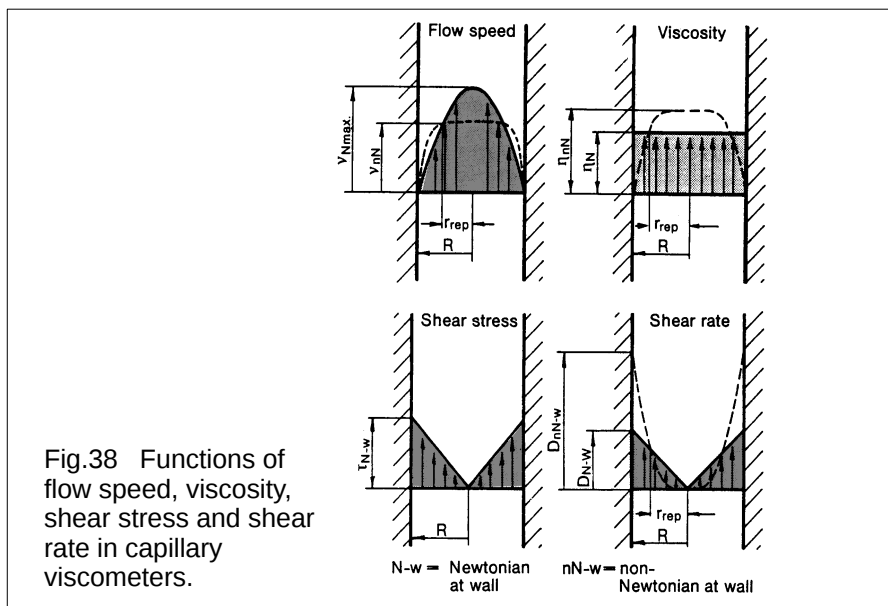
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Polymer melts are typical visco-elastic materials: higher shear rates create the usual shear stresses but also normal stresses, which show up as swelling of the extrudate coming out of the die and as a phenomenon called “melt fracture”.

The determination of the shear rate at which the above mentioned phenomena become predominant is often very valuable in classifying the processability of samples. If one only requires absolute viscosity data, one has to select test conditions which keep the melt well below that critical shear rate to maintain a steady state and laminar flow conditions within the capillary. It is possible to extract relative elasticity data from extruder rod capillary rheometry if the die swell of the extrudate is gauged by an optical laser beam sensor and the swollen extrudate diameter is compared to the diameter of the die orifice. As new volume elements flow through the capillary all the time and as the time of passing from the pressure port I to port II is short, no such sample volume element can be maintained at a defined shear for any extended period of time. Capillary viscometers therefore cannot determine the transient properties of samples such as a thixotropic behavior or give insight into a shear and temperature related degradation of polymer melts.

B. Equations

They are given to allow the calculation of shear rate, shear stress and viscosity when working with round and slit cross-section capillaries.



The continuous lines in Fig. 38 indicate the conditions for Newtonian liquids [N] while the broken lines define non-Newtonian flow [nN].

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a. Round cross section capillaries, pipes etc.

(1) Shear stress τ

$$\tau_R = \left(\frac{R}{2 \cdot \Delta L} \right) \cdot \Delta P = C_1 \cdot \Delta P [\text{Pa}] \quad [23]$$

$$\tau_r = \frac{r}{2 \cdot \Delta L} \cdot \Delta P [\text{Pa}]$$

τ_R = shear stress at the radius R [Pa]

τ_r = shear stress at the radial coordinate r [Pa]

R = radius of the capillary wall [m]

r = coordinate in the radial direction [m]

ΔL = capillary length between points I and II [m]

ΔP = pressure drop along the capillary length ΔL [Pa]

C_1 = instrument constant related to the capillary dimensions. $\rightarrow \frac{R}{2 \cdot \Delta L}$

(2) Shear rate $\dot{\gamma}$

$$\dot{\gamma}_R = \frac{4}{\pi \cdot R^3} \cdot Q = C_2 \cdot Q [\text{s}^{-1}] \quad [24]$$

$$\dot{\gamma}_r = \left(\frac{4}{\pi \cdot r^3} \right) \cdot Q [\text{s}^{-1}]$$

$\dot{\gamma}_R$ = shear rate at the radius R [s^{-1}]

$\dot{\gamma}_r$ = shear rate at the radial coordinate r [s^{-1}]

Q = flow rate [m^3/s]

C_2 = instrument constant related to the capillary dimensions [m^{-3}] $\rightarrow \frac{4}{\pi \cdot r^3}$

(3) Viscosity η

Knowing τ and $\dot{\gamma}$ the dynamic viscosity η can be calculated making use of equation [2].

$$\eta = \frac{\tau_R}{\dot{\gamma}_R} = \frac{C_1 \cdot \Delta P}{C_2 \cdot Q} [\text{Pa} \cdot \text{s}] = \left(\frac{\pi \cdot R^4}{8 \Delta L} \right) \cdot \frac{\Delta P}{Q}$$

$$\eta = C_3 \cdot \frac{\Delta P}{Q} [\text{Pa} \cdot \text{s}] \quad [25]$$

C_3 = instrument constant combining C_1 and C_2 - it is related only to the dimensions of the capillary $\rightarrow$ term within the bracket ().

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Capillary Viscometry Means:

Preset a pressure value ΔP and measure the resulting flow rate Q , or preset a flow rate Q and measure the resulting pressure ΔP . Knowing the instrument constant C_3 then allows the determination of the viscosity η . Equation [25] is known as the “Hagen-Poiseuille” equation, which is valid only for liquids showing a Newtonian flow behavior. For them the viscosity is independent of the radius r , i.e. it is constant across the diameter.

b. Slit capillary of flow channels

(1) Shear stress

$$\tau_w = \left(\frac{h}{2 \cdot \Delta L} \right) \cdot \Delta P = C_1 \cdot \Delta P [Pa] \quad [26]$$

τ_w = shear stress at the wall [Pa]

h = slit thickness (m), being very small in comparison with the slit width w .

w = slit width (m).

C_1 = instrument constant $\rightarrow$ term within the bracket.

(2) Shear rate

$$\dot{\gamma}_w = \left(\frac{6}{w \cdot h^2} \right) \cdot Q = C_2 \cdot Q [s^{-1}] \quad [27]$$

$\dot{\gamma}_w$ = shear rate at the wall [s^{-1}]

C_2 = instrument constant $\rightarrow$ term within the bracket.

(3) Viscosity

$$\eta = \left(\frac{w \cdot h^3}{12 \cdot \Delta L} \right) \cdot \frac{\Delta P}{Q} = C_3 \cdot \frac{\Delta P}{Q} [Pa \cdot s] \quad [28]$$

C_3 = instrument constant related to the capillary dimension $\rightarrow$ term within the bracket ().

Inasmuch as capillary rheometry is predominantly used for polymer melts or other highly non-Newtonian fluids the use of the Hagen-Poiseuille-equation without corrections (Bagley- and Weissenberg/Rabinowitsch) would lead to errors in the evaluation of the true viscosity data on the order of 20 or more %. For comparing similar batches rheologically as in many cases of industrial quality control it is often sufficient to use the “apparent”, non-corrected data. A separate chapter, no. 9, on “corrections” deals with the above mentioned corrections.

3.2.3 Gravity force capillary viscometers – Model II of Fig.35

This type of viscometer differs from model I shown in Fig. 35 and 36 by the fact that the liquid sample is not subjected to high variable pressures but that it runs through the capillary by its own weight. The sample is filled into an upper wide reservoir which leads to the entrance of the capillary. The weight of the liquid column above the exit orifice equals the potential energy of the sample which forces the liquid to flow through the capillary.

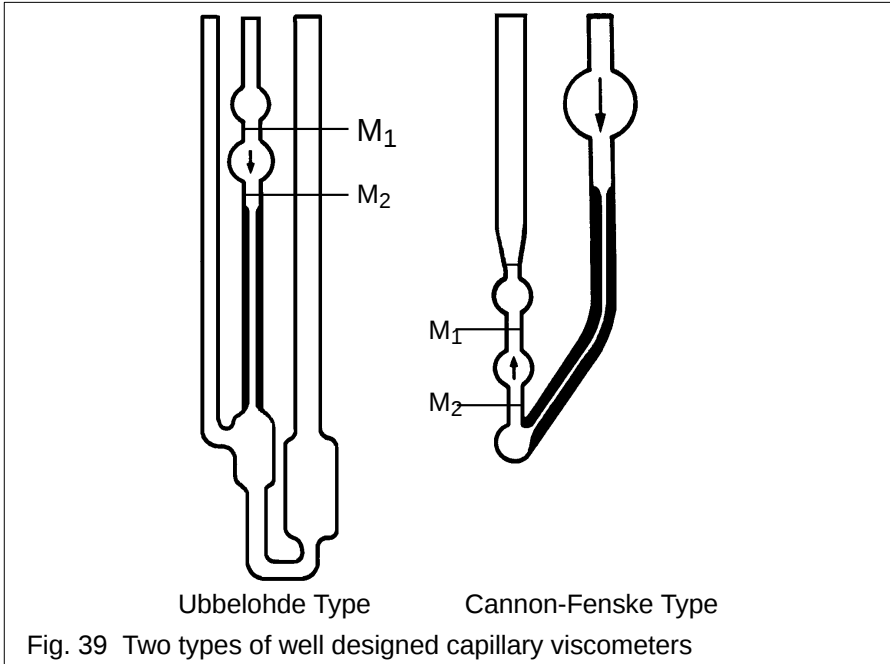


Fig. 39 Two types of well designed capillary viscometers

The measurement of viscosity with a viscometer such as an Ubbelohde viscometer requires measuring the time Δt it takes for a certain amount of liquid to pass through the capillary, or for the liquid level to drop between the markers M₁ and M₂. As the density of the sample is an important parameter, the test results measured come in units of kinematic viscosity ν – see chapter 2.5.

$$\nu = C_4 \cdot \Delta t \left[\frac{mm^2}{s} \right] \quad [29]$$

Δt = viscosity related time period

C_4 = instrument constant related to the dimensions of the capillary

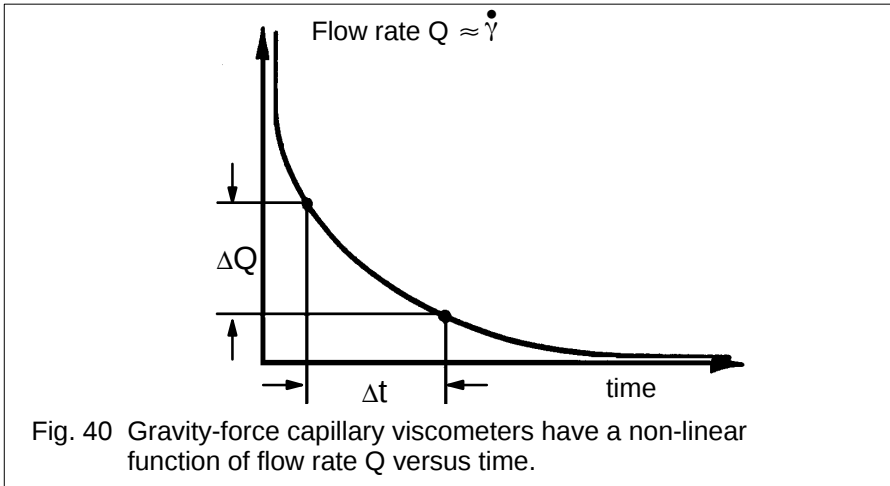
The Cannon-Fenske viscometer was designed to allow the measurement of non-transparent or dark Newtonian liquids. The time Δt for the liquid level to climb from M₁ to M₂ is measured.

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Good capillary viscometers such as Ubbelohde or Cannon-Fenske models have a long capillary length L and a small capillary diameter D . In order to minimize the error effects of non-laminar, not yet steady-state flow in the entrance to the capillary etc. ratios of $L/D = 30/1$ or larger are common. Ubbelohde type viscometers can be automated by using timers and printers.

Please note: The liquid level above the exit orifice slowly decreases during the time period Δt , which consequently causes the flow rate Q to drop with time:



Equation [23] indicates that the flow rate Q and the shear rate while linearly related are non-time dependent on each other, so that this gradual change of flow rate within a given time span also means a non-constant shear rate within that time period – Fig. 40. As a consequence of this statement the kinematic viscosity value ν measured in gravity-force capillary viscometers cannot be linked to one defined shear rate but to a more or less wide shear rate range. This is of no importance for shear rate-independent samples, i.e. Newtonian liquids, but this undefined shear rate excludes the use of gravity force capillary viscometers for liquids which show a distinct non-Newtonian behavior in the shear rate range relevant for these capillary viscometers.

Conclusion

Well designed gravity force capillary viscometers are excellent absolute viscometers for Newtonian liquids of low to medium viscosity. For the measurement of the viscosity of samples such as water, solvents or drinkable liquids Ubbelohde-type viscometers by far out-perform even the most sophisticated rotational viscometers/rheometers with respect to accuracy.

3.2.4 Melt indexers – Model III of Fig. 35

These are relatively simple capillary viscometers mainly used to grade the viscosity of polymer melts.

The polymer is melted in a cylindrical reservoir and then extruded out of the exit orifice by means of a plunger carrying one or more dead weights – Fig. 41. The exit orifice is really a capillary with a very short length (ratio of $L/D = 10/1$ or smaller). This capillary length is insufficient to guarantee the boundary conditions – constraints of rheometry – of steady state and laminar flow between the entrance of the capillary and the exit orifice. A sizeable amount of the potential energy in the system – here mainly the dead weight on the plunger – must be used to accelerate the sample to the flow speed at the exit and to overcome turbulence at the entrance to the capillary. Exit effects must also be accounted for inasmuch as the extrudate leaving the die transports kinetic energy with it which was not present when the sample entered the entrance region of the capillary.

Viscosity is measured by determining the volume of a sample that is extruded through the capillary within a defined time period Δt .

Test results gained with melt indexers and polymer melts can vary up to 30% from the corrected, true values obtained using capillary type viscometers with a high L/D -ratio such as in Fig. 36.

Melt indexers are customarily used for non-Newtonian polymer melts to determine their processability in production machines. However, shear rates in melt indexers are several decades below those encountered i.e. in dies of extruders or nozzles of injection molding machines. It is never a good idea to use viscosity values measured at low shear rates and then extrapolate to viscosity values linked to high shear rates if samples such as polymer melts are highly non-Newtonian.

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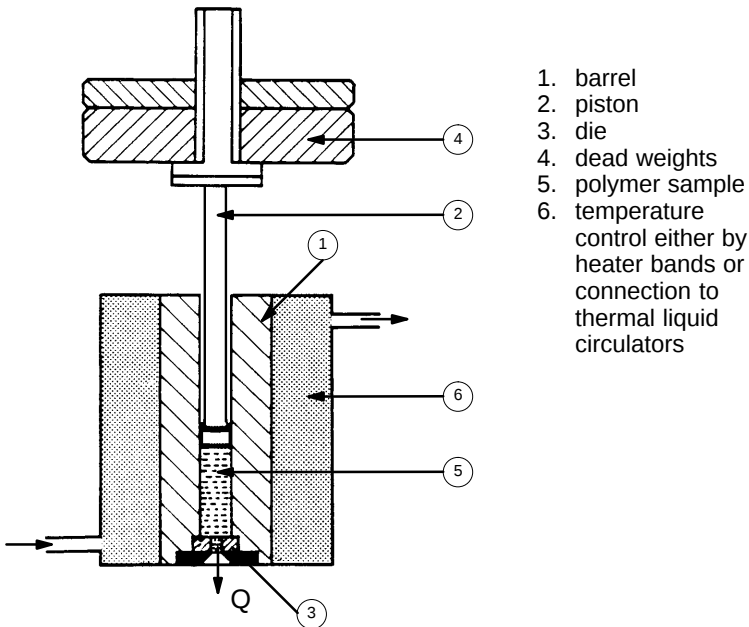
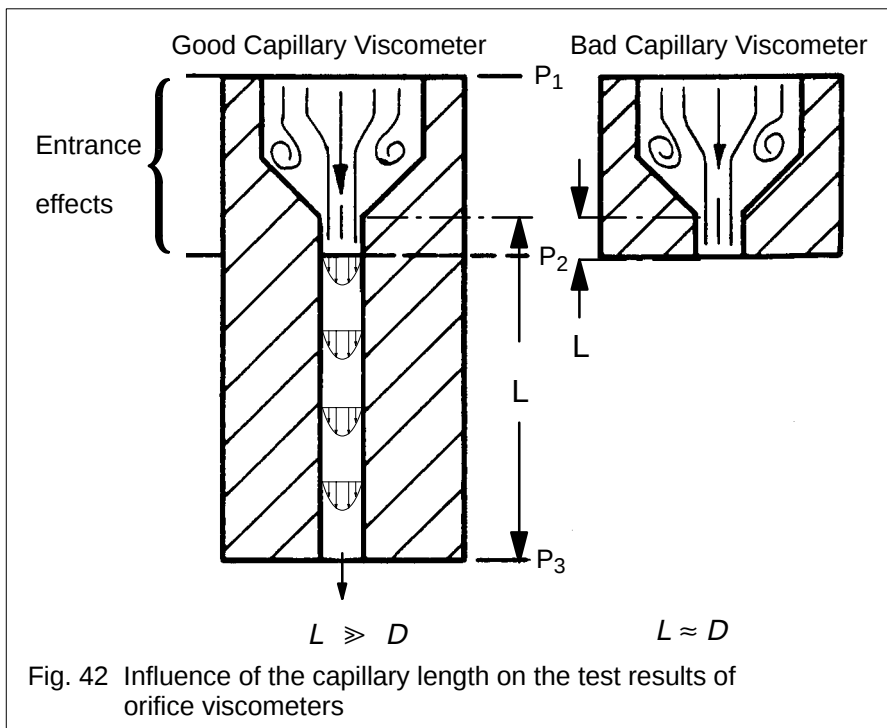


Fig. 41 Schematic drawing of a melt indexer

As the result of their relative low price, melt indexers are still quite common in industry for the testing of polymers with a relatively simple processing behavior such as polyethylene or polystyrene but they are losing popularity in the laboratories of companies which have to maintain high levels of quality control for raw materials and compounds.

Melt indexers may cause one other problem: if pelletized polymers are molten statically only by heat transfer from the heated barrel during 5 to 10 min the polymer may already start to chemically degrade before the actual start of the test. Bad test results can also be expected if the extrusion takes place before the polymer is not fully molten and when air has been entrapped in the melt. This will not happen with modern extruder capillary rheometers which use single or even twin-screw extruders to melt and homogenize polymers and their compounds and which will provide a melt of much higher homogeneity in a fraction of the time which melt indexers require.

3.2.5 Orifice viscometers – Model IV of Fig. 35



They are in principle also gravity force rod capillary viscometers which may be used for the testing of Newtonian fluids. They were used for very many years in the paints industry i.e. for fluids such as paints which are highly non-Newtonian, thixotropic and are best with small yield values. Only stirring the paint with a stick can be regarded as an inferior “viscometer” for paints.

But these Ford-Cup orifice viscometers are not even good viscometers for a Newtonian liquid: They feature very short capillaries which in certain cases simply become holes at the bottom of the liquid reservoir. The influence of the capillary length on test results is important. A sizable amount $P_1 - P_2$ of the total pressure differences $P_1 - P_3$ is consumed to accelerate the volume elements to flow through that hole and to overcome turbulence in the entrance to the capillary. Only when $P_2 - P_3$ is big in relation to $P_1 - P_2$ i.e. when the L/D ratio is 40/1 or larger the negative effects of the entrance disturbances are that much minimized to provide true viscosity data. Simple orifice viscometers have a pressure drop $P_1 - P_2$. This means that they measure only entrance

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effects which are “somehow” viscosity related. The test results can only be used to classify e.g. a series of oil samples on a relative basis.

Models such as Engler, Saybolt or Redwood beakers are typical instruments: Ford or DIN cups are illustrated in Fig. 43 below.

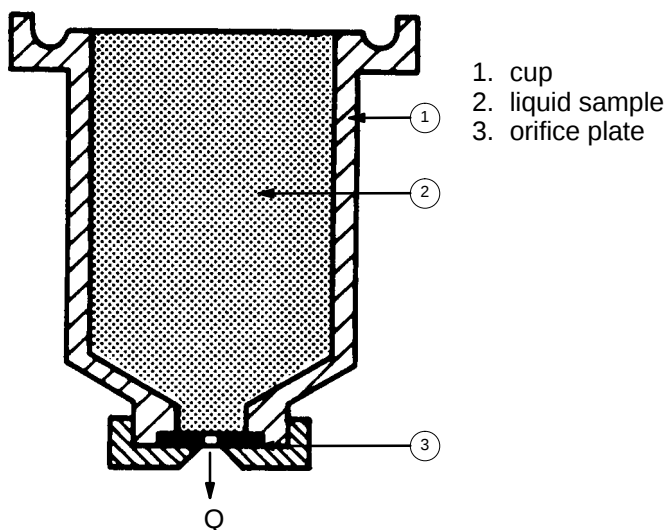


Fig. 43 Schematic drawing of a simple orifice viscometer

All of these cups and beakers are subject to the overwhelming errors linked to the entrance and exit effects. While the Engler beaker is relatively good with an $L/D = 10/1$, even so $3/4$ of the pressure drop within the liquid is used for the acceleration of the liquid. This leaves just $1/4$ of the pressure drop to be linked to viscous flow. The principle of the Engler beaker is seen when comparing the viscosity of an unknown liquid with the viscosity of water at 20°C . With a Newtonian sample of ten times the viscosity of water, the flow rate in a Ubbelohde viscometer would drop to $1/10$, but in an Engler apparatus to only $1/2$, in comparison to the flow rates encountered with water. This indicates the errors encountered with the Engler beaker.

Orifice viscometers are from a rheological standpoint “quite miserable”. Even for Newtonian liquids one cannot find reasonable correlations to absolute viscometer data.

3.3 The Falling Ball Viscometer

Most common is the Hoesppler Falling Ball Viscometer – Fig.44 –, which is named after the HAAKE chemist who invented it in the Thirties. It is a simple, but still very accurate viscometer for the viscosity measurement of transparent fluids ranging from gases to liquids of low to medium viscosity. This viscometer has even today its place in industry and in research especially for the measurement of low viscosity Newtonian liquids such as beverages or human blood plasma. The variation of the diameter and/or the density of balls easily changes the measuring range of this viscometer. The standard sample volume is approx. 40 cm³.

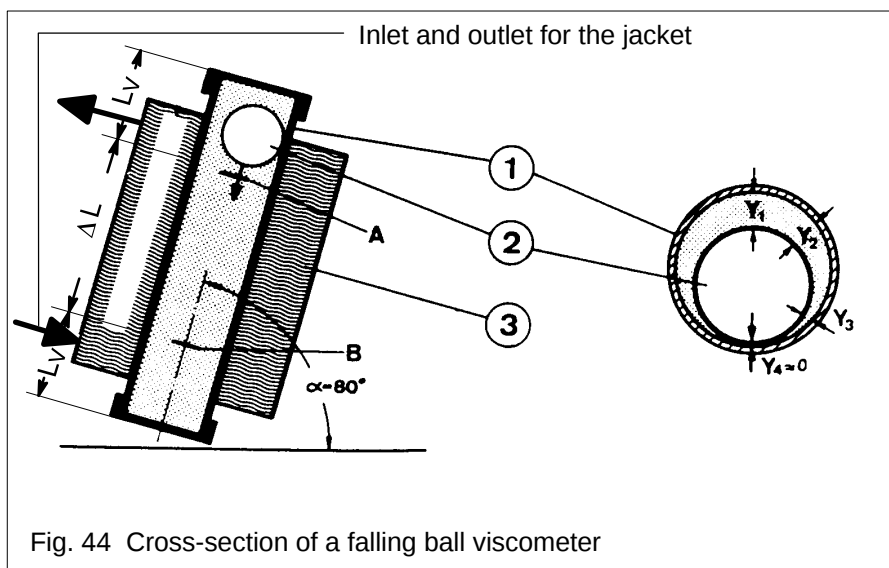


Fig. 44 Cross-section of a falling ball viscometer

A fluid sample – in almost all cases it is liquid – is contained in a glass measuring tube (1) surrounded by a jacket (3) to allow an accurate temperature control by means of a constant temperature circulator. This tube is positioned in a 10° inclination with respect to the vertical. The tube has two ring marks A and B spaced apart by $\Delta L = 100$ mm. A ball (2) is allowed to fall through the fluid sample. Falling from the starting position (speed $v = 0$) at the top of the tube the ball first accelerates along the distance L_V to allow the ball to reach a steady-state speed providing a uniform shear flow of the liquid in the sickle-shape gap surrounding the ball. The time Δt required for the ball to pass between the two ring marks A and B is measured. The value Δt can be used to calculate viscosity in the absolute units of [mPa·s]. The instrument is calibrated by means of Newtonian liquids of known viscosity.

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The viscosity η (mPa·s) is calculated using the equation:

$$\eta = k \cdot (\rho_1 - \rho_2) \Delta t \quad [30]$$

k = instrument calibration factor [mPa · cm³/g]

ρ_1 = density of the ball [g/cm³]

ρ_2 = density of the liquid sample [g/cm³]

Δt = time span for ball to fall the distance ΔL [s]

Application:

To decide whether this instrument can successfully be used for Newtonian liquids as well as for non-Newtonian liquids it is worthwhile to look at the cross-section of the tube and the ball which form a sickle-shaped gap for the fluid to pass through.

The 10° inclination of the tube guarantees that the ball always touches the tube on one side. The values y_4 to y_1 indicate that the gap size varies along the circumference of the ball. Inasmuch as the shear rate links the flow speed to the gap size, it is evident that a constant shear rate within the whole sickle-shaped gap does not exist. When the ball falls and the fluid flows around the ball, the fluid is subjected not to a single value of shear rate but to quite a wide shear rate range.

The conclusion of this statement is:

Falling ball viscometers can be used with very good success for all liquids, whose flow behavior does not depend on the shear rate, i.e. it should **only** be used for Newtonian liquids. The undefined conditions in the sickle gap prohibit the use of falling ball viscometers for non-Newtonian liquids for which any viscosity value is almost useless unless it is linked to the relevant shear rate.

An advanced version of the falling ball viscometer uses medical glass syringes as falling tubes and gold plated steel balls. The required sample volume consists of only 0.3 cm³. A magnet which is rotated at a constant speed and passes behind the syringe lifts the ball twice every minute. When the magnet rotates further out of the way of the ball, this ball can freely fall through the liquid. Passing through two light diode switches the speed of the ball can be timed as a digital Δt signal. Thus every 30s the magnet returns. It lifts the ball and a new time value replaces the old one on the LCD-display. This cycle may be continued endlessly but at least as long as to reach an equilibrium time value. Connected to a computer, this miniature falling ball viscometer (HAAKE Microviscometer) allows one to monitor the uniformity of the test results against time and provide tabulated test protocols of e.g. a patient's plasma viscosity and a mean standard deviation for the test point variation.

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A variation of the falling ball viscometer is the drawn ball viscometer (HAAKE Viscobalance).

A ball attached to a rod can be pulled upwards through a liquid contained in a measuring tube. This viscometer measures viscosity by determining the time Δt the ball requires to pass the two ring marks A and B on the measuring tube.

This modification of the falling ball viscometer is used especially for the viscosity measurement of non-transparent liquids and highly viscous fluids even at high temperatures, however the limitation with respect to the requirement of a Newtonian flow behavior is true also for this instrument. Inasmuch as especially the cleaning of this Viscobalance at the end of a test is messy and laborious, those who can afford a cone-and-plate rotational rheometer will prefer the latter.

4. The Measurement of the Elastic Behavior of Visco-elastic Fluids

4.1 Why measure elasticity?

In the introduction it was stated that materials could either show a solid or a liquid behavior depending on their characteristic time factor " λ " **and** on the process related time value " t ". With the Deborah-number being either high or low a material may show a predominantly solid- or liquid-like behavior. Viscosity and elasticity are two sides of a material's property to react to imposed stresses.

When we look at everyday processes such as applying paints, mixing food-stuffs, chewing gum or shaping polymer melts in extruder dies or rapidly filling the moulds of injection moulding machines, we see that under these conditions many fluids are distinctly visco-elastic, i.e. they exhibit both viscous **and** elastic properties. For some processes the elastic behavior is the dominant factor prohibiting higher production rates while for other processes such as settling of fillers in a suspension with a continuous phase of high viscosity, the zero shear viscosity will be the governing factor.

Knowing where and how fluids are used or processed by measuring the visco-elastic response of batches under process related test conditions is of great value for quality control applications: are the fluids more viscous than elastic or vice versa?

Polymer research has clarified the molecular structure of many types of polymer melts and how modifications of that structure will influence their rheological behavior in steady-state or dynamic tests. This knowledge can then be used to deduce the specific molecular structure from the rheological test results of new melt batches.

Placing special emphasis on the determination of the elastic properties of a fluid – while not neglecting the viscous ones – gives scientists an excellent insight into its molecular structure and will enable them to modify this structure to meet special application requirements. In that respect modern rheometers can well compete with other research instruments for e.g. gel permeation chromatography. One can additionally state that rheology, e.g. in comparison to GPC, requires less time to get significant data.

4.2 What causes a fluid to be visco-elastic?

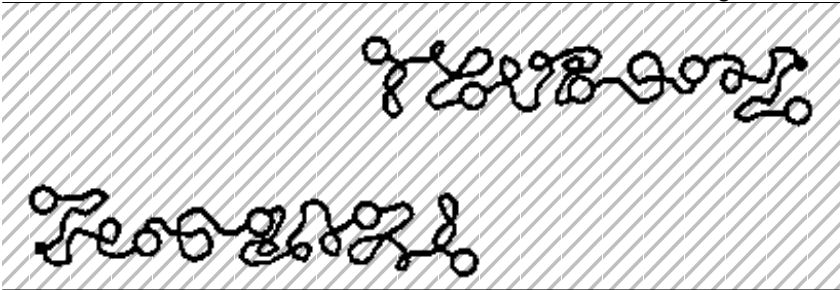
A.) Many polymeric liquids, being melts or solutions in solvents, have long chain molecules which in random fashion loop and entangle with other molecules. For most thermoplastic polymers carbon atoms form the chain

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backbone with chemical bond vectors which give the chain molecule a random zig-zag shape. These molecules maintain a minimum energy-state – entropy – at rest. A deformation will stretch the molecule or at least segments of such a molecule in the direction of the force applied. Stretching enlarges the bond vector angles and raises as a secondary influence the energy state of the molecules. When the deforming force is removed the molecules will try to relax, i.e. to return to the unstretched shape and its minimum energy state. Science has provided quite a number of molecule models to explain linear and non-linear visco-elasticity which cannot be discussed here in detail. One of them is the bead-spring model of Rouse-Zimm.

a.) Long-chain molecules in a knurled interlooped state in such a low concentration in a solvent that molecules do not entangle.



b.) as above: but molecules are reduced to spring elements and beads.

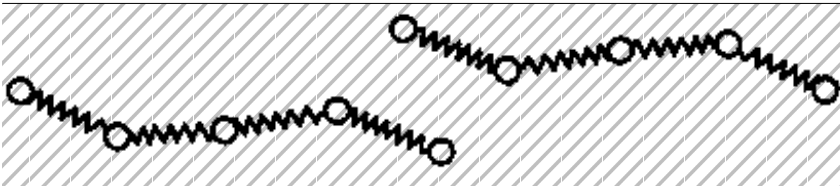


Fig. 45 Rouse-Zimm model for a visco-elastic fluid using springs and beads.

The beads are supposed to provide the sites of the fluid friction – the viscous component – while the springs connecting the beads introduce the intramolecular elastic behavior – Fig.45. Being stretched they are able to temporarily absorb and store part of the deformation energy, thus increasing their entropy.

B.) These long chain molecules do not act alone in an empty space but millions of similar molecules interloop and entangle leading to an intramolecular interaction – Fig.45. Non-permanent junctions are formed at entanglement points leading to a more or less wide chain network with molecule segments as connectors.

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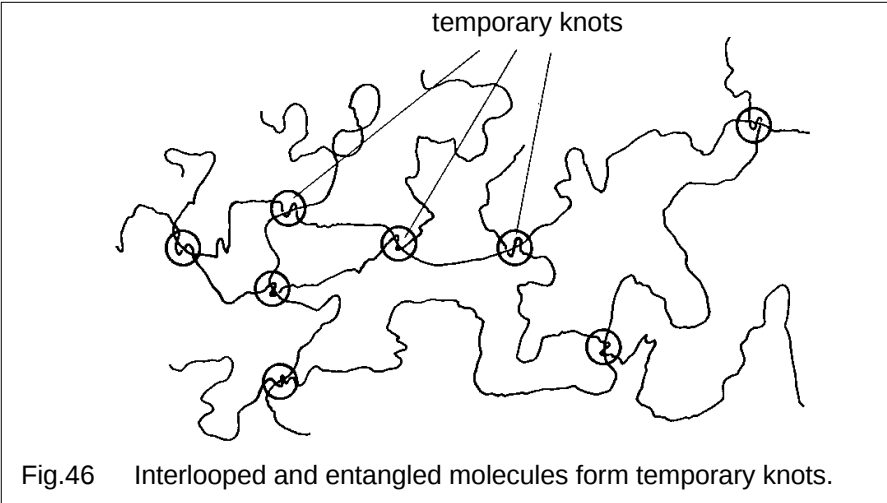


Fig.46 Interlooped and entangled molecules form temporary knots.

When subjected suddenly to high shearing forces the fluid will initially show a solid-like resistance against being deformed within the limits of the chain network. In a second phase the connector segments will elastically stretch and finally the molecules will start to disentangle, orient and irreversibly flow one over the other in the direction of the shearing force. This model image of a polymer liquid makes its viscous and elastic response understandable and also introduces the time-factor of such a response being dependent initially more on elasticity and in a later phase more on viscosity. One other phenomenon is worthwhile mentioning: When small forces are applied the molecules have plenty of time to creep out of their entanglement and flow slowly past each other. Molecules or their segments can maintain their minimum energy-state because any partial stretching of spring segments can already be relaxed simultaneously with the general flow of the mass. At slow rates of deformation polymer liquids show a predominantly viscous flow behaviour and normally elasticity does not become apparent. At high rates of deformation an increasingly larger part of the deforming energy will be absorbed by an elastic intra- and intermolecular deformation while the mass is not given time enough for a viscous flow. Together with an elastic deformation, part of the deforming energy is stored which is recovered during a retardation/relaxation phase. This partially retracts molecules and leads to a microflow in the direction opposite to the original flow. Deformation and recovery are time dependant – transient – processes, which require attention and which will be dealt with in the following chapters.

C.) Human whole blood is another example of a visco-elastic fluid, which is a dispersion of elastic corpuscular cells – mainly erythrocytes (red blood cells) – in an almost Newtonian plasma. These red cells of coin-like shape form large aggregates – rouleaux – in large blood vessels. when the blood flows slowly,

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i.e. at a low shear rate and consequently the blood viscosity is high. With increasing flow rates in smaller blood vessels the rouleaux, which resemble stacks or rolls of many coins – these rouleaux even branch – are broken up into the individual red cells with a diameter of approximately $d = 8 \mu$. This results in the whole blood viscosity being drastically reduced.

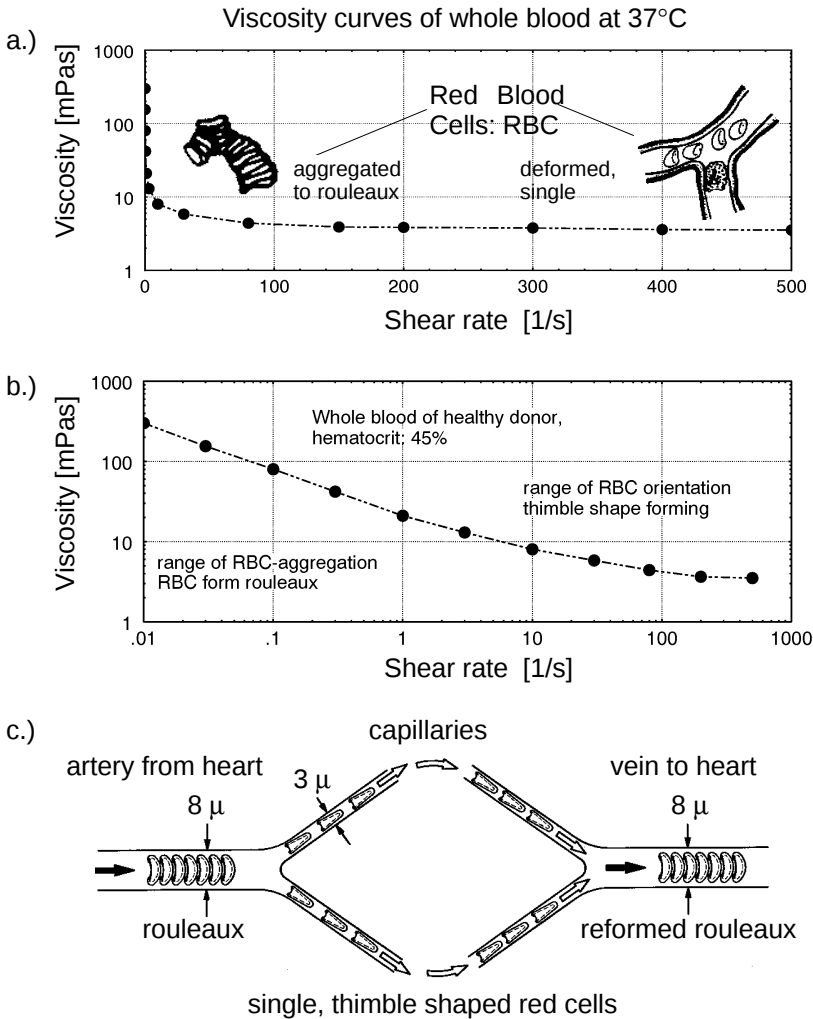


Fig. 47 Whole blood viscosity influenced by red cell aggregation and elastic red cell deformation

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Fig. 47a. indicates the dramatic increase of viscosity of whole blood at shear rates close to $\dot{\gamma} = 1$ 1/s. Fig. 47b is logarithmically scaled to indicate better flow behavior at low shear rates: viscosity can increase 100-fold for a four-decade shear rate change. Fig 47c schematically indicates that red cells continuously cycle between aggregated clusters in larger blood vessels and singular deformed cells when passing through small capillaries in the passage from arteries to veins.

Since the capillaries which provide the link between arteries and veins are only some 3 microns wide, the red cells are able to elastically deform until they reach a thimble shape which meets the 3 microns inner diameter of the capillary. Once these thimbles again reach the larger diameter veins they “spring-back” to their flat coin shape. It is the reversible deformability – elasticity – at a high shear of the corpuscular blood cells and their ability to aggregate at low shear that gives whole blood its unique visco-elastic flow behavior. *Without it human beings and other mammals depending on blood circulation for the metabolism for the body cells could not survive.*

D.) Distinct elastic properties are characteristic for polymer blends such as natural caoutchouc NR with synthetic rubber SBR1500, which combine these two or more polymers differing in their physical and chemical properties. Polymer blends are almost never homogeneous solutions such as “sugar in tea” but there are always corpuscular volume elements of the higher molecular weight polymer dispersed in the continuous phase of the other lower viscous polymer.

As an example of a typical polymer blend enlarged photographs of microtome slices – Fig.48: unknown origin – indicate the more or less heterogeneous dispersion of butadiene rubber volume elements – black – in an ABS continuous mass:

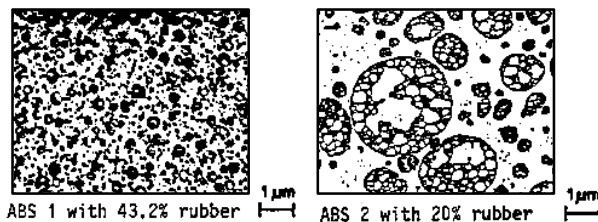


Fig.48 The rheological and processing properties of these ABS blends depend largely on the dispersion and elasticity of the dispersed particles in the continuous phase. (Photographs of microtome cuts of unknown origin).

Dispersions should be as homogeneous as possible, but it is difficult to break-up and disperse components of tough and highly elastic NR in a much

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lower viscous mass. Such a rubber blend might be compared to a “pea soup” with many whole peas swimming in a watery soup. One could stir this soup “for ages” with a spoon without meshing-up the peas because the individual peas can always escape the action of the spoon by “swimming” sideways. Blending rubbers in large internal mixers often leads mainly to a mastication – molecular weight reduction by mechanical shear – of the lower viscous continuous phase while leaving the individual dispersed NR-particles almost intact. Being tough and elastic these particles are often just temporarily stretched during mixing and they recover their initial shape shortly after having passed the gap between rotor and mixer wall.

The ability to mix is not only important with respect to the major two polymer components but even more so when further compound ingredients such as sulfur, carbon blacks or lubricants are added and which in a non-suitable mixing process will be found predominantly in the continuous phase. This heterogeneity of such a polymer compound greatly affects the vulcanized final product such as a rubber tire. Elastically frozen-in stresses in polymer blends can only retard in the long-term – at least minutes but more often in hours – because this will require a microflow of stretched molecules or of dispersed volume elements against the resistance of the surrounding continuous mass, which at almost zero-shear viscosity provides a very high resistance against this microflow.

This example demonstrates clearly how the visco-elastic behavior of a dispersion or blend influences its processability and its quality as a finished product. Only measuring both viscosity and elasticity of raw rubbers and their blends under near-production conditions of variable shear intensity and shear time will allow one to characterize these highly elastic masses, determine rheologically their dispersion homogeneity and to find optimized processing conditions

4.3 How to measure visco-elasticity

Having given examples of typical visco-elastic fluids we will now concentrate on the question, how the combined property of viscosity and elasticity is best measured. We start with two phenomena caused by elasticity which can be used to actually measure this rheological behavior:

4.3.1 The Weissenberg effect

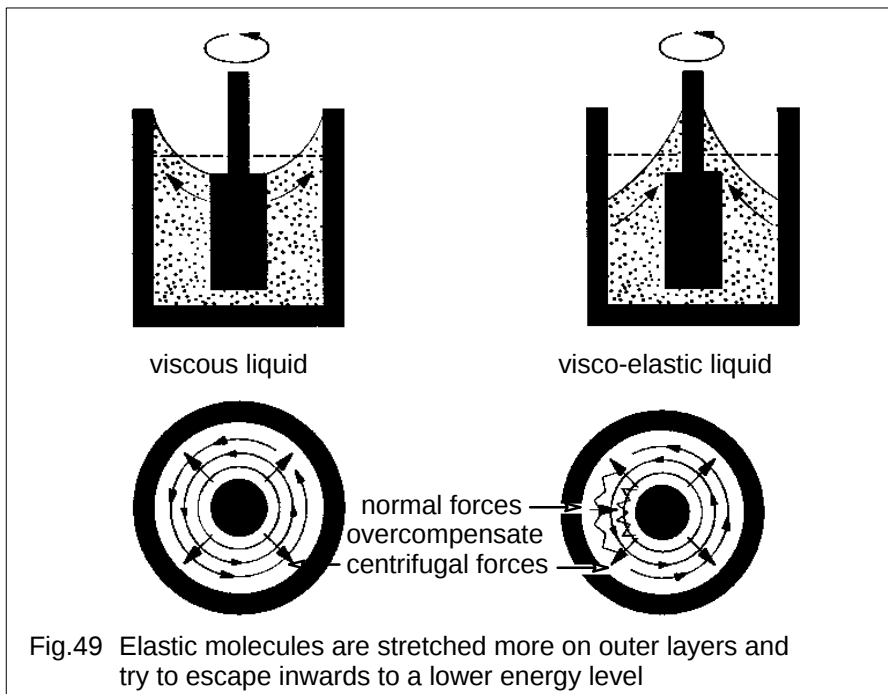
A. A general description of the phenomenon

Fig. 11 has already shown the difference between a Newtonian and a visco-elastic liquid when they are stirred by a rotor in a pot. While the Newtonian liquid as the result of centrifugal forces is thrown outwards and upwards against the wall of the pot, the visco-elastic liquid is drawn up the rotor shaft against the force of gravity. This phenomenon can be seen typically when mixing flour and water to make bread- or cake dough – Fig. 50.

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Using the above model image of a visco-elastic fluid will help one to understand what causes the fluid to climb up the rotor shaft – Fig1 49.



The continuously rotating rotor will create concentric layers of the liquid with decreasing rotational speeds inwards-outwards. Within those layers the molecules will have disentangled and oriented in the direction of their particular layer and being visco-elastic one can assume that molecules on the outer layers will be stretched more than those nearer to the rotor. A higher degree of stretching also means a higher state of energy from which molecules will tend to escape. There is one possibility of escape for those stretched molecules by moving towards the rotor axis. If all molecules move inwards it “gets crowded” there and the only escape route is then upwards.

Rotation thus causes not only a shear stress along the concentric layers but also an additional stress – a normal stress – which acts perpendicular to the shear stress. This normal stress forces visco-elastic liquids to move up rotating shafts and it creates a normal force trying to separate the cone from its plate or the two parallel plates in rotational rheometers . Fig.50 shows the well-known phenomenon of dough – flour mixed with water – being forced up the shafts of mixer rotors.

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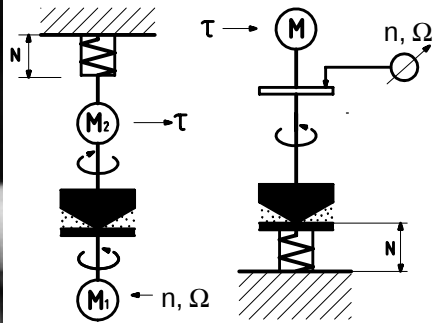
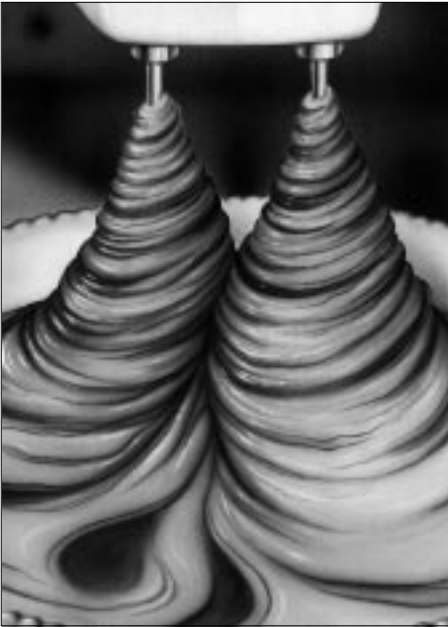


Fig.50 left – Mixed dough climbs up rotating shafts
above – measuring both shear stress τ and normal force N with a CR-Couette- and a CS-Searle measuring system

The visco-elasticity of a fluid tested in a cone-and-plate sensor system is similarly the cause for the normal force, which with increasing rotational speed sucks the liquid out of the gap and up on the outer rim of the cone. This will result in the liquid sample splitting in the gap ending any meaningful test. Prof. Weissenberg noticed the phenomenon caused by elasticity which was named after him. He used it for the Couette-type Rheogoniometer which he designed: In addition to a shear stress sensor, he designed a sensor for measuring normal stress. In this second sensor the rotor shaft is positioned on an axially acting measuring spring, the deflection of which is a measure of the axial force F_n proportional to the normal stress N created in the visco-elastic liquid.

Today there are quite a number of competing rheometers of the Searle- and the Couette-type on the world market, which still use this principle for normal stress measurements: In Couette rheometers the upper cone-and-plate-axis rests on the normal force detector – Fig.50, center. In Searle rheometers a suitable pressure sensor can be incorporated in the lower stationary plate. The normal force detector must be very stiff to prevent an axial displacement of the “spring” to widen the gap size between the cone and plate which would otherwise result in sizable errors. This is especially dangerous if cones with small angles are used. Sophisticated rheometers use compensating methods to keep the gap size constant and independent of the magnitude of any normal force. – Fig.50, right side.

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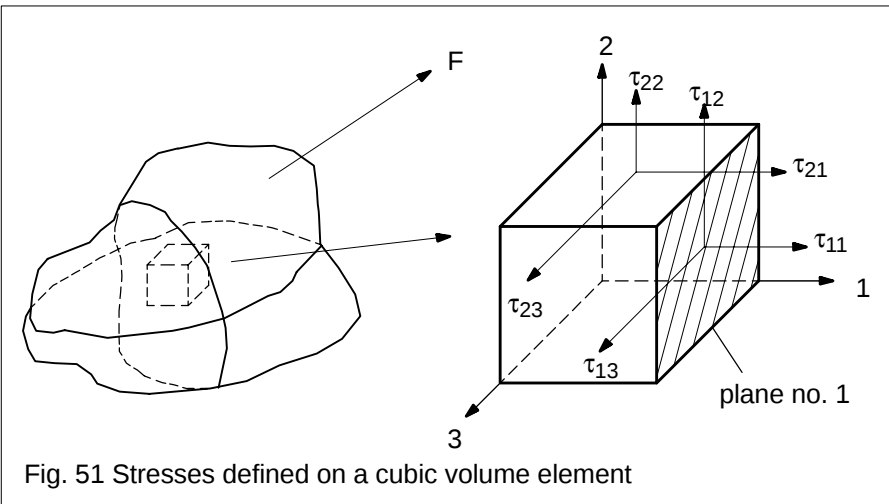
The need to characterize the elastic behavior of many fluids such as polymer solutions or melt adhesives has created a lot of interest in normal stress measurements. But one has to be aware of one important drawback: just this elasticity which one aims to measure causes inevitably this splitting of the sample sheared in the cone-and plate – Fig. 33 at high shear rates. This phenomenon, called the “Weissenberg effect”, limits the use of cone-and-plate- and parallel-plate-sensor systems of rotational rheometers for the rheological testing of visco-elastic fluids to relatively low shear rates rarely surpassing $\dot{\gamma} = 100$ to 200 1/s. One usually does not approach the shear rates which are encountered in i.e. capillary rheometry.

Please note:

For the viscosity measurement of non-elastic liquids the cone-and-plate sensor system can be safely used for shear rates up to $\dot{\gamma} = 10\,000$ 1/s – if one can cope with shear heating.

B. Definition of Normal Stresses and Normal Stress Differences

If a force F acts on a body containing a cubic volume element, it results in a deformation of this body. The total stress on such an inner volume element can be broken up into 9 different stress components – 6 shown – as indicated in Fig. 51.



One can differentiate for any plane that forms the cube between the “normal stress” components which act perpendicular and the “shear stress” components which act tangentially.

It is common to refer to the shear stress components as τ_{ij} , where the first subscript “i” refers to the plane the stress acts on (the i-plane is the plane for

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which the normal stress is acting in the i-direction) and the second subscript "j" indicates the direction of the stress component.

A stress component is said to be positive when it acts in the direction of the coordinate axis. All stresses can be combined in a stress tensor:

$$\tau = \begin{bmatrix} \tau_{11} & \tau_{12} & \tau_{13} \\ \tau_{21} & \tau_{22} & \tau_{23} \\ \tau_{31} & \tau_{32} & \tau_{33} \end{bmatrix}$$

This tensor can be simplified:

a.) $\tau_{ij} = \tau_{ji}$, which leaves 6 independent stress components.

b.) in the case of incompressible fluids the absolute values of the three normal stresses do not influence the deformation of the fluid. The deformation depends only on the difference between the normal stresses and the isotropic pressure, or what is the same, on the difference between the three normal stresses.

When normal stress differences are utilized, only two are necessary to fully describe the influence of all three normal stresses on the deformation.

In the general case of the deformation of incompressible fluids the stress within the fluid is fully described by only three shear stresses:

τ_{12} (equal to τ_{21})

τ_{13} (equal to τ_{31})

τ_{23} (equal to τ_{32})

and the two normal stress differences:

$N_1 = (\tau_{11} - \tau_{22})$

$N_2 = (\tau_{22} - \tau_{33})$

In the special case of an ideal shear flow which is approximated in the parallel-plate-, the cone-and-plate-, and in the coaxial cylinder sensor systems, the shearing deformation is applied in such a way that τ_{13} and τ_{23} are zero. In this case the total stress in the fluid is described by:

$\tau_{12} \rightarrow$ the shear stress

$N_1 = (\tau_{11} - \tau_{22}) \rightarrow$ the "first normal stress difference"

$N_2 = (\tau_{22} - \tau_{33}) \rightarrow$ the "second normal stress difference"

N_1 provides the axial pressure against cone and plate, N_2 is related to the pressure variation within the gap as a function of the radius.

In order to describe the fluid property as a function of the rate of deformation – in the case of shear flow: shear rate $\dot{\gamma}$ – only the following three functions are needed:

the viscosity:

$$\eta(\dot{\gamma}) = \tau_{12} / \dot{\gamma} \quad [31]$$

the "first normal stress coefficient": $\psi_1(\dot{\gamma}) = (\tau_{11} - \tau_{22}) / \dot{\gamma}^2 = N_1 / \dot{\gamma}^2 \quad [32]$

the "second normal stress coefficient": $\psi_2(\dot{\gamma}) = (\tau_{22} - \tau_{33}) / \dot{\gamma}^2 = N_2 / \dot{\gamma}^2 \quad [33]$

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In the case of a liquid showing a Newtonian flow behavior both $\psi_1(\dot{\gamma})$ and $\psi_2(\dot{\gamma})$ are zero. Such a liquid in an ideal shear flow is therefore rheologically fully described by its viscosity $\eta = \text{constant}$

C. Measurement of the Normal Stress Differences.

a.) Cone-and-plate sensor systems

The normal stress difference N_1 can be determined by the measurement of the normal force F_n which tries to separate the cone from the lower plate when testing visco-elastic fluids:.

$$N_1 = 2 \cdot F_n / \pi \cdot R^2 \text{ [Pa]} \quad [34]$$

the shear rate is: $\dot{\gamma} = \Omega / \alpha$

F_n = normal force acting on the cone in the axis direction [N]

R = outer radius of the cone [m]

Ω = angular velocity [rad/s]

α = cone angle [rad]

b.) Parallel-plate sensor systems

With the parallel-plate sensor system one determines the difference between the two normal stress differences:

$$N_1 - N_2 = (2 \cdot F_n / \pi \cdot R^2) \cdot [1 + 1/2 \cdot d \ln F_n / d \ln \dot{\gamma}_R] \quad [35]$$

$$\dot{\gamma}_R = \Omega \cdot R / h$$

h = distance between the plates

R = outer radius of the plate

F_n = the normal force acting on the plate in the axial direction.

The difference $N_1 - N_2$ refers to the shear rate $\dot{\gamma}_R$ at the outer radius of the plates. If one uses a cone-and-plate sensor system for the determination of N_1 and the parallel-plate configuration for the measurement of $(N_1 - N_2)$ utilizing in each case the same $\dot{\gamma}_R$, then one can calculate N_2 by combining the two measurement results.

The second normal stress difference N_2 is generally very small in comparison to N_1 . It is said to have a negative value. The measurement of N_2 requires very elaborate testing with specially built rheometers and the time effort for this testing is considerable.

The measurement of N_1 is indeed very meaningful to explain processes such as coating melt adhesives onto boards and one can normally do without knowing N_2 . It is generally accepted to transform the measured normal force F_n to just N_1 instead of $(N_1 - N_2)$ when making use of parallel-plate sensor systems.

Typical measurement results of a number of visco-elastic samples with a rheometer featuring a normal force sensor are given in the following diagrams:

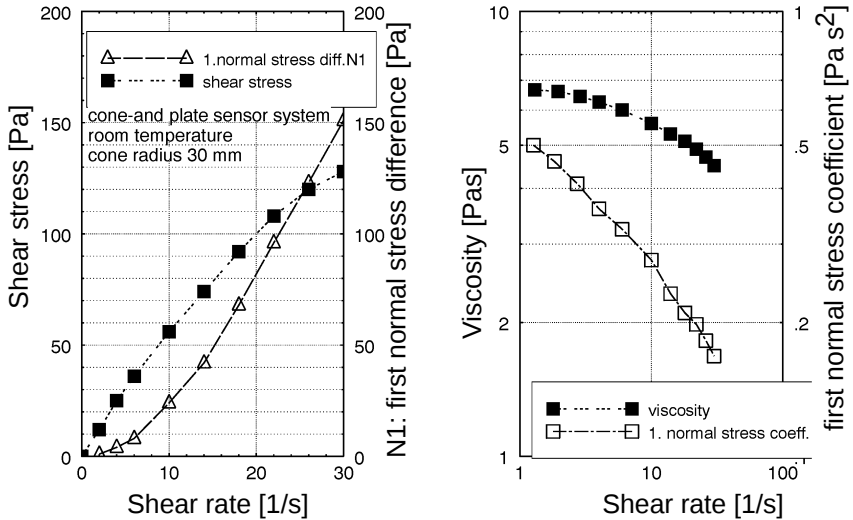


Fig. 52 Testing the visco-elastic behavior of a bubble soap

Fig. 52 indicates for a bubble soap sample that at low shear rates the shear stress is a decade larger than N_1 , but that this relationship between τ and N_1 reverses already at a $\dot{\gamma}_R > 25$ 1/s: the rheological behavior of this sample is then more influenced by its elastic than by its viscous properties. When this happens one can expect that the elastic behavior of this sample becomes too strong resulting in a partially emptied shear gap. Programming the shear rate to increase further will provide meaningless test results. Software allows one to convert the measured data of τ and N_1 to η and ψ_1 . The slopes of both curves indicate that at lower shear rates than those used for this test the 1. normal stress coefficient ψ_1 will surpass the viscosity η . This is in line with literature which reports that for very low shear rates the value of ψ_{10} exceeds η_0 .

$$\psi_1 = N_1 / \dot{\gamma}^2 \text{ [Pa} \cdot \text{s}^2\text{]}$$

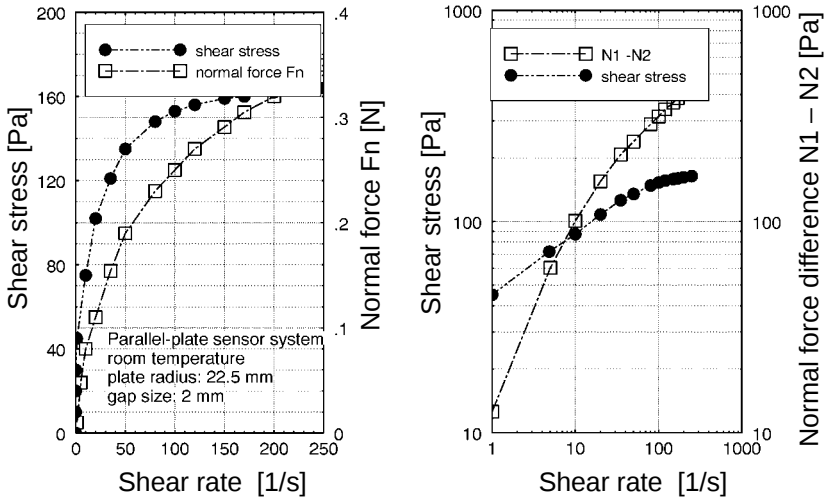


Fig. 53 Testing the visco-elastic behavior of a pharmaceutical jelly

Fig. 53. describes similar results – this time a parallel-plate sensor system was used – for a pharmaceutical jelly which features a strong yield value: the two diagrams in linear and logarithmic scaling both indicate how the elastic component surpasses the viscous one at quite low shear rates.

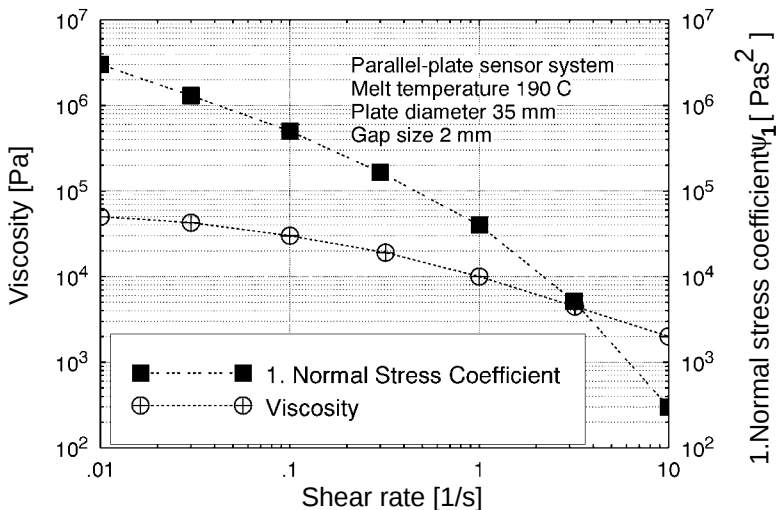


Fig. 54 Testing the visco-elastic behavior of a PE-melt

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Fig. 54 plots the curves of viscosity η and of the first normal stress coefficient ψ_1 as a function of the shear rate for a polyethylene melt tested in a parallel-plate sensor system. This diagram already covers 3 decades of shear rate, but this is still not sufficient to indicate that for still lower values of shear rate both η and ψ_1 will reach constant values of η_0 and ψ_{10} . Testing the viscous and the elastic properties of such a polymer melt at low or even very low shear rates presents difficult technical problems especially for the measurement of normal forces. They are of such a small magnitude that the normal force detectors are not be sensitive enough to provide significant data. As it will be detailed in chapter 9, it is possible to make use of the method of the WLF-superposition by testing the melt sample at several temperatures. The resulting family of viscosity- and normal stress coefficient curves forms a “master-curve” that covers as in Fig. 54 not just three but six decades of shear rate.

The testing of both shear and normal stresses at medium shear rates in steady-state flow characterizes samples under conditions of the **non-linear** visco-elastic flow region, i.e. conditions which are typical of production processes such as coating, spraying and extruding. For these processes the elastic behavior of high molecular weight polymers such as melts or solutions is often more important than their viscous response to shear. Elasticity is often the governing factor for flow anomalies which limit production rates or cause scrap material.

The measurement of η and N_1 describes the visco-elasticity of samples differently in comparison to dynamic tests which are designed for testing in the **linear** visco-elastic flow region as it is explained in the following.

For very small deformation rates ($\dot{\gamma}_R$ and ω) the 1. normal stress difference $1N_1(\dot{\gamma}_R)$ can be equalled to the storage modulus $G'(\omega)$ of a dynamic test:
 $\lim 1/2 \cdot N_1(\dot{\gamma}_R) / \dot{\gamma}_R^2 = \lim G'(\omega) / \omega^2$ for both $\dot{\gamma}_R$ and ω approaching zero.

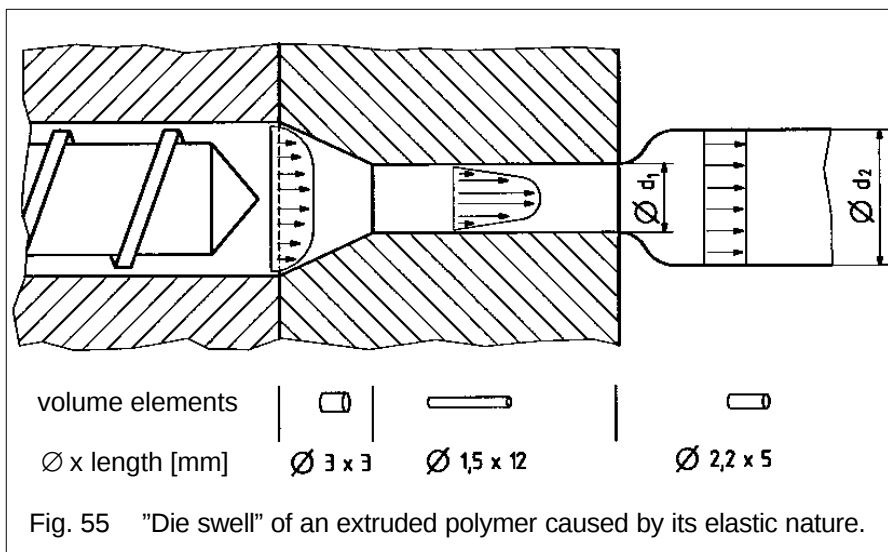
It should be just mentioned that the 1st normal stress difference is generally a transient value. When applying a constant shear rate value and plotting the development of N_1 versus time the resulting curve will approach the stationary value only after some time. Only in the linear visco-elastic flow region are both N_1 and ψ_1 are independent of the shear time.

4.3.2 "Die swell" and "melt fracture" of extrudates

Extruding polymer melts often leads to extrudates with a much wider cross-section in comparison to the one of the die orifice. Fig. 55 indicates that a cylindrical volume specimen in the entrance region to the die/capillary is greatly lengthened and reduced in diameter when actually passing through the capillary.

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A sizable amount of the potential energy-pressure present in the entrance region to force the melt through the capillary is used for the elastic stretching of the molecules which store this energy temporarily until the melt is allowed to exit at the capillary end. Here – at ambient pressure – the melt is now free to relax. The volume element regains its diameter and it shrinks in length. The percentage of die swell – extrudate cross-section/die cross-section – increases with the extrusion rate and it has been shown to correlate to other elasticity measurements in different testing set-ups. The die swell testing is a relative measure of elasticity able to differentiate different types of polymers or compounds. The extrudate thickness is gauged by means of laser light beams which having passed the extrudate are hitting a light sensor plate. The thicker the extrudate the less light is reaching the light sensor. The extrudate die swell is normally measured close to the extruder die when the melt is still fully molten and therefore able to swell but under those conditions not enough time is provided for a full recovery of the elastically stored energy within the short time for the extrudate to pass from the die to the position of the die swell tester.

Die swell tests may not be a perfect method to measure elasticity in comparison to rotational rheometers and e.g. their normal force measurement. But die swell tests provide meaningful relative elasticity data at shear rates that may reach up to 5000 1/s or even more at which no other elasticity measurement can be performed.

For highly elastic melts at high extrusion rates the extrudate can show a very distorted, broken-up surface, a phenomenon known as “melt-fracture”. For each polymer a limit for an elastic deformation exists above which oscillations within the melt appear. They cannot be sufficiently dampened by the internal friction of this visco-elastic fluid and therefore lead to an elastic-turbulent melt flow. This appearance of melt fracture at a flow rate specific for a particular melt and a given set of extrusion conditions is an important limit for any die swell tests. Going beyond this point means erratic, useless elasticity and viscosity data.

4.3.3 Creep and recovery

4.3.3.1 Description of the test method

Under this name a test method for visco-elasticity has been introduced, which allows one to differentiate well between the viscous and the elastic responses of a test specimen. In comparison to the normal force measurement, which marks the shear rate dependency of viscosity and elasticity, the creep and recovery measurement introduces the additional parameter of “response time” to the stress-dependency of both the viscous and the elastic behavior of solids and fluids.

The method of testing can be explained by simple examples:

a.) Elastic response

Knocking with a hammer on a piece of vulcanized rubber this hammer will shortly dent the rubber surface but due to the rubber being fully elastic the hammer will be thrown up again and the dent in the rubber surface will almost momentarily disappear: the rubber surface becomes repaired, i.e. the elastic deformation is fully recovered.

In instrumental terms such a test could be run with a disk-shaped rubber specimen positioned in a parallel-plate sensor system of a rotational rheometer:

Applying a constant shear stress τ_0 on the upper plate the specimen is twisted. The angle of such a twist is defined by the spring modulus of the vulcanized rubber. If stress and the resulting deformation are linearly linked then doubling the stress will double the deformation. This rubber specimen being twisted acts in a similar manner as a metal spring which is expanded or compressed by a load. The deformation is maintained as long as the stress is applied and the deformation disappears fully and instantaneously when the load is removed. The energy of deformation is elastically stored in the spring or the rubber specimen and it may be recovered 100% when the load is removed. The schematic of this load/deformation versus time is given by the open-triangle-line in Fig. 52.

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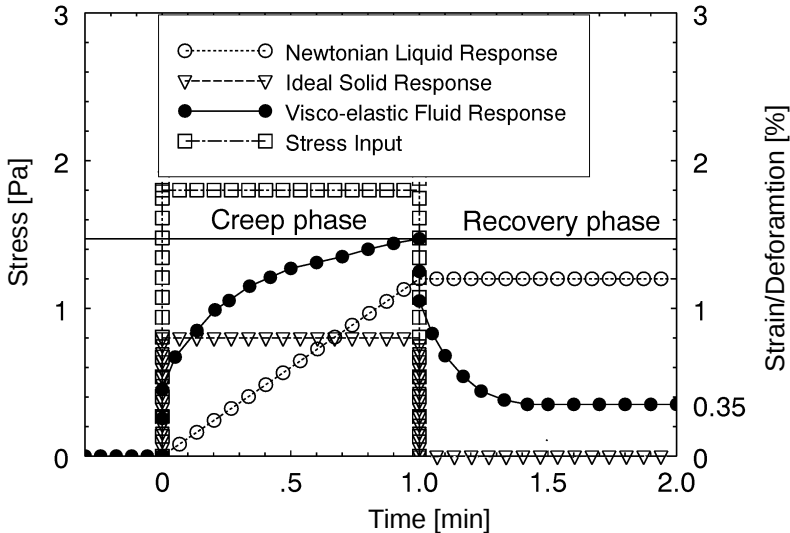


Fig. 56 Stress and strain responses of several typical samples

b.) Viscous response

A totally different behavior is apparent when water is poured out of a bottle onto a flat table surface. The water forms a water puddle on the table which flows outwards until the water layer has become very thin: only the surface tension of the water prevents the water layer at the rim of the puddle from becoming infinitesimally thin. The kinetic energy of water hitting the table surface and the gravity on upper water layers in the puddle force the water to flow. When this energy has been used up the water "stays put". Not being elastic, water will never flow back into the bottle by itself. The energy that made the water flow is fully transformed into shear heat, i.e. this energy cannot be recovered.

Placing a water specimen similarly into a parallel-plate- or cone-and-plate-gap of the sensor system, applying stress and plotting the resulting deformation of this water sample with time shows a linear strain being unlimited as long as the stress is applied. When the stress is removed the deformation is fully maintained (see the open-circle line in Fig. 56.)

c.) Visco-elastic response

Visco-elastic liquids which have been pictured as a dispersion of molecules with intermittent spring-type segments in a highly viscous oil show a behavior which is somehow in between the stress/deformation responses of those two

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examples being either fully elastic or fully viscous. When a stress is applied instantaneously the fluid may react with several time-related phases of strain – see the black-dot line in Fig.56: initially by some spontaneous elongation of some spring segments positioned parallel to the applied stress. Then the other spring segments and the network between temporary knots will deform within their mechanical limits resisted and retarded by the surrounding viscous continuous mass. Finally the molecules may disentangle and participate in the general flow. While in the early phase of the creep test the elastic components can stretch to their mechanical limits, they will then float within the matrix mass when the stress is maintained longterm: the sample shows now a viscous flow.

Plotting the strain response as a function of time, the deformation shows initially a rapid often steplike increase which is followed by a gradually decreasing slope of the strain curve. This curve may finally lead within some minutes or even longer asymptotically into a tangent with a constant slope: the fluid is now showing a fully viscous response to the applied stress.

If the sample is a visco-elastic solid subjected to a stress below the yield value the strain curve will eventually approach asymptotically a constant strain level parallel to the time abscissa: under these conditions there is some elastic deformation but no flow.

During the creep test of visco-elastic fluids the stress applied will cause a transient response which cannot be broken up clearly into the overlapping elastic and the viscous contribution. It is the advantage of the following recovery phase after the release of the applied stress that it separates the value of the total strain reached in the creep phase into the permanently maintained viscous part and the recovered elastic part (see also Fig. 56).

The recovery as well as the earlier creep phases are time-dependent. To determine the above viscous and elastic percentages accurately requires relaxation times of infinite length. In practical tests of most fluids one can observe the recovery curve until it has sufficiently levelled within 5 to 10 min on that viscosity related constant strain level. For very high molecular weight polymers such as rubbers below 100°C this recovery phase can be as long as hours. Going back to the model picture of molecular spring segments in a viscous surrounding it seems understandable that the deformed springs want to return to their fully released shape during the recovery. They can only do so against the retarding action of the viscous surrounding, which must allow some microflow in the opposite direction of the initial deformation. This microflow being very slow with a shear rate that can be lower than 10^{-6} 1/s provides an almost zero-shear – i.e. a very high viscosity which then has the consequence of up to hourly relaxation times.

Still a new aspect for the evaluation of visco-elasticity needs to be mentioned here: linear visco-elasticity.

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In steady-state-flow boundary conditions were introduced to define test conditions allowing one to measure material constants such as the dynamic viscosity. One of the boundary conditions was the requirement of laminar flow. Changing test conditions by i.e. increasing rotor speeds to the extent, that laminar flow was forced to turn into turbulent flow meant a reactionary torque which can easily be twice or more than the one encountered with the undisturbed laminar flow. This torque linked to turbulence can no longer be related to a material constant: It is greatly influenced by the test procedure – rotor speed – and the test apparatus. The data that result from such a test outside the boundary conditions may still be of some use for a relative comparison of samples tested under the same conditions, but they cannot be considered as absolute rheological data.

In visco-elasticity we encounter similar limits for the proper use of the rheometer. We distinguish between linear- and non-linear visco-elasticity. In the former it is required that the applied stress leads to a proportional strain response: Doubling the stress will double the strain. The theory of linear visco-elasticity provides linear differential equations, which can be solved for constants being material parameters. Changing the test conditions by i.e. choosing very high stresses leading to non-proportional strains will provide elasticity and viscosity data which are greatly influenced by the chosen set of test parameters and the geometries of the sensor system. These data may still serve for the comparison of different samples, but they are not absolute data for a material, which could be duplicated in any other suitable rheometer. In creep tests a constant stress is assigned and the time-related strain is measured. The two can be mathematically interrelated by:

$$\gamma(t) = J(t) \cdot \tau \quad [36]$$

This equation introduces the new term of the time-related compliance $J(t)$. It is a material function similar to the viscosity η in steady-state-flow. It defines how compliant a sample is: the higher the compliance the easier the sample can be deformed by a given stress. The compliance is defined as:

$$J(t) = \gamma(t)/\tau \quad [1/\text{Pa}] \quad [37]$$

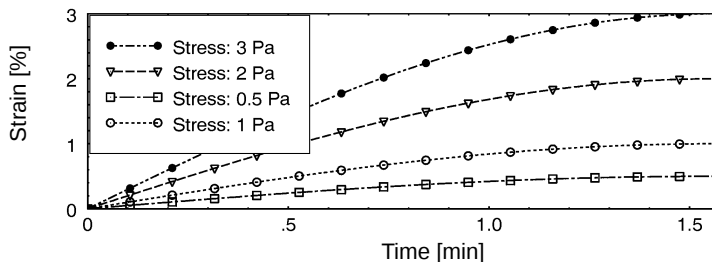
As long as the tested sample is subjected to test conditions which keep the stress/strain interaction in the linear visco-elastic region, the compliance will be independent of the applied stress.

This fact is used for defining the limits for the proper creep and recovery testing of visco-elastic fluids within the limits of linear visco-elasticity.

The same sample is subjected in several tests – Fig. 57 – to different stresses being constant each time during the creep phase. The result of these tests will be strain/time curves which within the linear visco-elastic range have strain values at any particular time being proportional to the stresses used.

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Family of Creep Compliance Curves related to Different Stresses

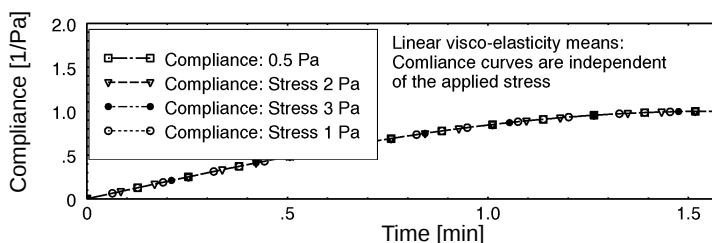


Fig. 57 Creep tests: Strain and compliance curves for visco-elastic samples subjected to variable stresses within the boundaries of linear visco-elasticity

Assuming that elasticity may be linked to temporary knots of molecules being entangled or interlooped the proportionality of stresses and strains may be understood as the ability of the network to elastically deform but keep the network structure as such intact. If one divides the strain values by the relevant stresses this will result in the corresponding compliance data. When plotting those as a function of time all compliance curves of the above mentioned tests will fall on top of each other as long as the tests comply with the limits of linear visco-elasticity.

When much higher stresses are used the above mentioned network with temporary knots is strained beyond its mechanical limits: the individual molecules will start to disentangle and permanently change position with respect to each other. In suspensions the van der Waals-intermolecular forces between molecules or volume elements may be strained beyond their limits allowing an irreversible flow of those molecules or volume elements with respect to each other: the sample increasingly is led to flow and reaching a high shear rate it shear-thins. Thus these higher stresses lead to a lower viscosity with the consequence that the deformation is more than proportion-

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ally increased. The slope of the strain/time-curve $\tan \alpha$, which marks the relevant shear rate, becomes steeper with increased stresses being applied: the increased slope is an indication of a reduced viscosity.

$$\dot{\gamma} = \tan \alpha = \tau/\eta \rightarrow \eta \text{ decreases when } \dot{\gamma} \text{ increases}$$

When this happens the compliance curves will start to deviate from those which had fallen on top of each other indicating that the chosen test conditions will provide non-linear visco-elastic data. These data are no longer material functions because they are greatly influenced by the test apparatus and the chosen test condition.

It should be noted, that generally the stresses that keep samples within their range of linear visco-elasticity are in most cases small. On this background it seems evident that real production processes subject visco-elastic fluids normally to conditions where non-linear visco-elasticity prevails – such as mixers are characterized by their turbulent flow and not only by laminar flow. Any rheological material testing should therefore explore how samples behave inside and outside the range of linear visco-elasticity – even if the latter results can only be used for a direct comparison of several similar samples subjected to a particular set of stress/strain-conditions.

4.3.3.2 Some theoretical aspects of creep and recovery tests.

Please note: the theory of creep and recovery and its mathematical treatment uses model substances such as springs and dashpot, either single or in combinations to correlate stress application to the time-dependent deformation reactions. While such a comparison of real fluids with those model substances and their responses cannot be linked to distinct molecular structures, i.e. in polymer melts, it helps one to understand visco-elasticity. Since this evaluation by means of the model substances is rather complicated and involves some mathematics, it has been combined in this chapter which the less theoretically-minded reader may prefer to omit: pages 99 to 107.

In order to understand time-dependent stress/strain responses of real visco-elastic solids and fluids which have a very complicated chemical and physical internal structure, it has become instructive to first look at the time dependent response to stresses of very much simpler model substances and their combinations. Grading the results of real visco-elastic samples on the background of similar results of model substances allows one to classify samples as visco-elastic solids or liquids. A correct interpretation of these test results will provide among others some insight into the time-scale required to reach meaningful test results or to optimize production procedures. Introducing some mathematical equations in this context seems unavoidable. They are given for users of rheometers to assure them of the sound physics background of test results.

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a.) The ideal solid – Fig. 58

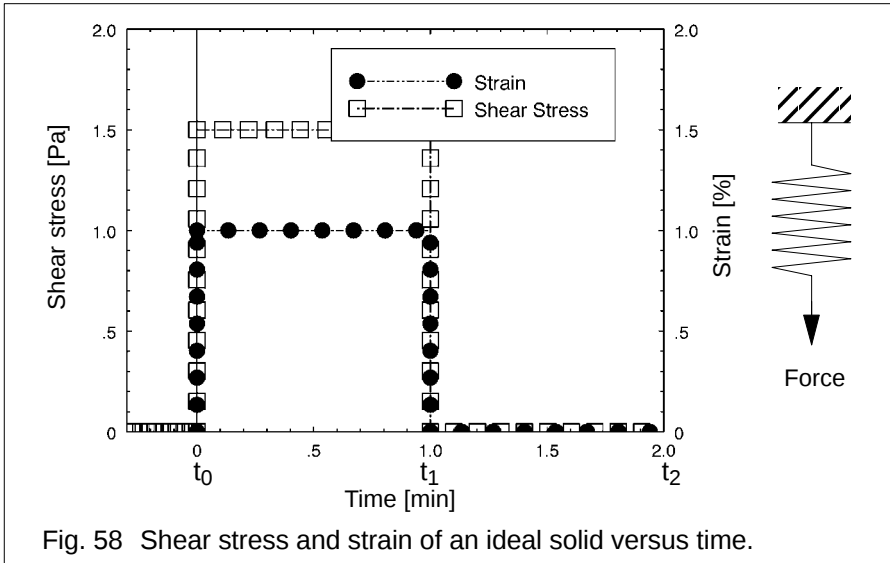


Fig. 58 Shear stress and strain of an ideal solid versus time.

In the chapter “Introduction” it was stated for an ideal solid that an application of a force or stress is instantaneously followed by a deformation/ strain, which is linearly proportional to the force applied: doubling the stress means doubling the deformation, which remains constant as long as that stress is applied. The ratio of strain and stress is a measure of the elasticity of the solid concerned. With the removal of the stress the deformed body springs instantaneously back to the original shape it had prior to the stress application. The interaction of forces and strains is totally reversible. A metal spiral spring is used as a model to typically characterize an ideal elastic body: force and extension are linearly linked. Forces applied may lead to tensile or shear stresses and the tensile modulus E (Young’s modulus) or the shear modulus G are the correlating factors representing the resistance of a solid against being deformed. These moduli are material constants for such a solid.

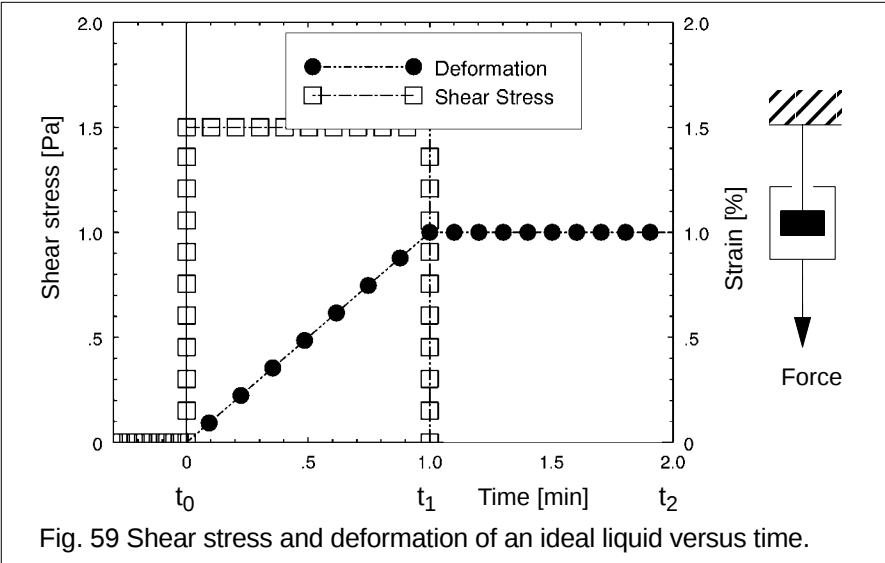
$$\begin{aligned}\sigma &= E \cdot \gamma \\ \tau &= G \cdot \gamma\end{aligned}$$

σ = tensile stress; τ = shear stress; γ = deformation
Both stresses and strains are non-time dependent.

b.) The ideal Newtonian liquid – Fig. 59

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Such a liquid is characterized by a behavior which linearly correlates a force applied to the rate of deformation. Liquids can only be subjected to shear stresses which when maintained permanently lead to a linearly increasing deformation with time. The final deformation is maintained when the stress has been removed. A damper or dashpot – a piston fitting in an oil-filled cylinder – is used to characterize the behavior of a Newtonian liquid: the force acting on the piston and the rate of the displacement of the piston defined by the Newtonian viscosity of the oil are linearly linked. The dynamic viscosity η , representing the resistance of the liquid against being forced to flow, is the correlating factor related to the nature of the liquid.

$$\tau = \eta \cdot \dot{\gamma} = \eta \cdot d\gamma/dt$$

c.1.) Combination of springs and dashpots to define visco-elasticity.

Using combinations of these models in series or in parallel, one can demonstrate typical properties of visco-elastic fluids and solids, and deduce mathematical equations for their force/deformation response. While a proven comparability of the responses of the various combination models to the actual rheological behavior of visco-elastic materials exists, such a comparison of mechanical models does not correlate with any particular characteristics of the internal molecular structure or the homogeneity of blends of real substances.

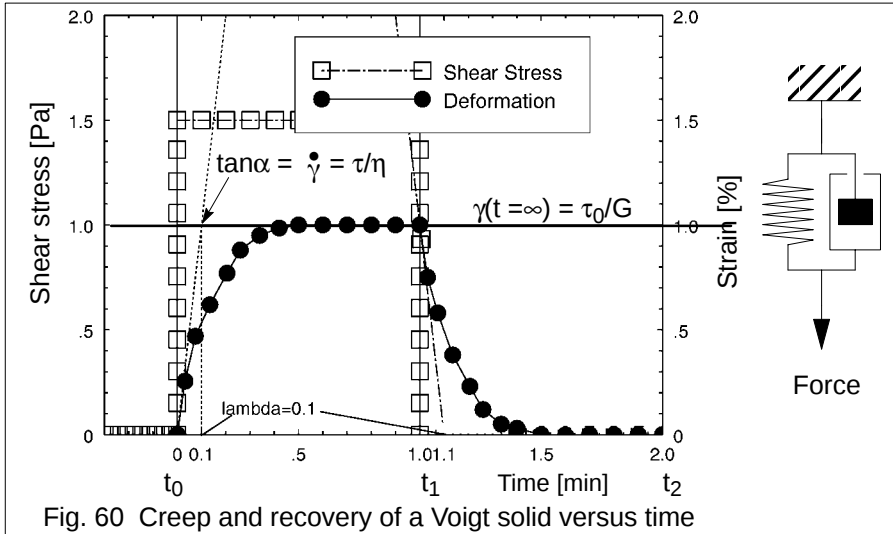
The combination of a dashpot and a spring will lead to a time-dependent response of the rheological parameters which does not exist for the single dashpot or spring. The type of links between the mechanical models will define whether one deals with a visco-elastic solid (Kelvin-Voigt solid) or a visco-elas-

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tic liquid (Maxwell liquid). These models are relatively simple inasmuch as they link only a single dashpot with a single spring. Equations are given for both models which fit the requirements of linear visco-elasticity. Real visco-elastic substances are represented by more complex combinations of springs and dashpots.

c.2.) Kelvin-Voigt solid – Fig. 60



It combines a spring and a dashpot in parallel: a rigid frame ensures that any force applied to the system is equally acting on the spring and on the dashpot.

The system ensures that:

The total strain γ is equal to the strain in the dashpot γ_V and equal to the strain of the spring γ_E :

The stress τ_0 applied is equal to the sum of the stresses in the dashpot τ_V and the spring τ_E . Substituting the equations of state for the elastic response of the spring and the viscous response of the Newtonian liquid leads to:

$$\tau = G \cdot \gamma + \eta \cdot d\gamma/dt \quad [38]$$

The solution of this differential equation at constant stress is:

$$\gamma(t) = \tau_0/G [1 - e^{(-t/\lambda)}] \quad [39]$$

$$\lambda = \eta/G = \text{relaxation time} \quad [40]$$

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Please note:

Strained sample can “relax” while the stress is maintained.
With the stress removed the recovery of the strain is “retarded”

When the time t becomes infinite this equation reduces to:

$$\gamma(t = \infty) = \gamma_{\infty} = \tau_0 / G \quad [41]$$

This is the final response of the spring. The action of the dashpot retards this response initially.

Once the stress is applied, the strain/time-curve increases initially with a slope that is related to the shear rate in the dashpot $\rightarrow \dot{\gamma} = \tau / \eta$.

Graphically λ is indicated by the intersection of the initial tangent on the strain curve and the parallel to the abscissa at $\gamma = \gamma_0$.

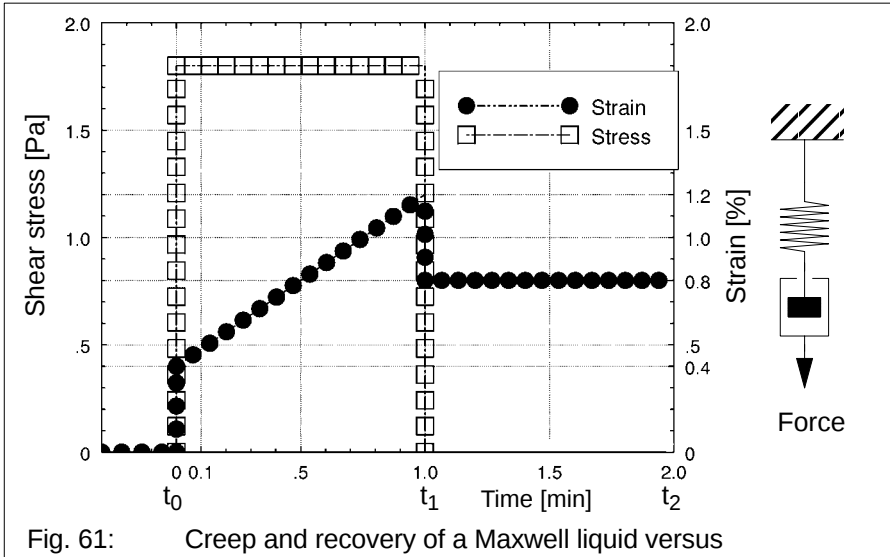
Having reached the steady-state strain level a removal of the stress will allow the Kelvin-Voigt model to fully recover: the strain reduces to zero following the equation:

$$\gamma = \gamma_0 \cdot e^{-[(t-t_1)/\lambda]} \quad [42]$$

When the time t becomes infinite, the strain reduces to zero, i.e. the solid sample fully recovers its original shape. The retardation times λ are equal in the creep and the recovery phases when conditions of linear visco-elasticity prevail.

Being an ideal solid means that volume elements do not irreversibly change place, i.e. the stress applied does not lead to any flow. The Kelvin-Voigt model represents a visco-elastic solid.

c.3.) The Maxwell fluid – Fig. 61



In this model substance the spring and the dashpot are placed in series, which has the consequence that the shear stresses in both elements are always identical and that the deformations are additive.

$$\tau = \tau_V = \tau_E \quad [43]$$

$$\gamma = \gamma_V + \gamma_E \quad [44]$$

The derivative of the strain is

$$d\gamma/dt = d\gamma_V/dt + d\gamma_E/dt$$

$$d\gamma/dt = \tau/\eta + 1/G \cdot d\tau/dt$$

This differential equation has the solution:

$$\gamma(t) = (\tau_0/\eta) \cdot t + \tau_0/G \quad [45]$$

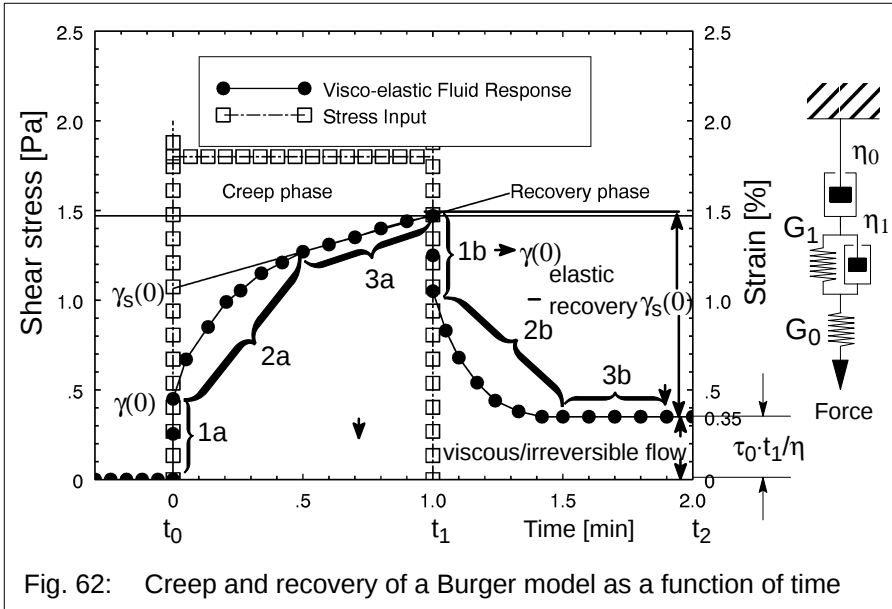
The Maxwell model characterizes a visco-elastic liquid. Subjected to an instantaneous step of a deformation force/stress this model reacts first with an instantaneous step of strain increase in accordance to the elastic response of the spring. In the later phase of the test the fluid shows a viscous response, i.e. the deformation is unlimited as long as the stress is applied and the strain proceeds to increase at a constant rate related to the viscosity of the dashpot liquid.

When the applied stress is instantaneously removed at the time t_1 , the strain drops immediately to a new time-constant level. This drop relates to the stress release of the spring while the remaining permanent strain is equivalent to the amount of the viscous flow during the creep phase.

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c.4.) The Burger model – Fig. 62



The two preceding models of a visco-elastic solid and a visco-elastic liquid are too simple for the assumption that real visco-elastic materials can be rheologically represented by either of the two. The Burger model with a Kelvin-Voigt solid and a Maxwell liquid linked in series to each other represents real materials much better.

This model is made up of 2 springs with the moduli G_0 and G_1 and two dashpots with the viscosities η_0 and η_1

The equations of state for the two constitutive components in series are:

$$\begin{aligned} \tau_1 &= G_1 \gamma_1 + \eta_1 \cdot d \gamma_1 / dt & \text{for the Kelvin-Voigt solid} \\ 1/G_0 \cdot (d\tau_0/dt) + \tau_0/\eta_0 &= d\gamma_0/dt & \text{for the Maxwell liquid} \end{aligned}$$

Since these components are in series the stress of each will be equal to the total stress and the total strain will be the sum of the strains on both components:

$$\begin{aligned} \tau &= \tau_0 = \tau_1 \\ \gamma &= \gamma_0 + \gamma_1 \\ d \gamma / dt &= d \gamma_0 / dt + d \gamma_1 / dt \end{aligned}$$

It can now be written:

$$\tau = G_1 \gamma_1 + \eta_1 d \gamma / dt - \eta_1 [1/G_0 (d\tau/dt) + \tau/\eta_0] \quad [46]$$

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The full mathematical evaluation of the Burger model leads to a rather complicated differential equation which can be solved for the creep phase:

$$\gamma(t) = \tau_0 \cdot t / \eta_0 + \tau_0 / G_0 + \tau_0 / G_1 [1 - e^{-(t/\lambda)^1}] \quad [47]$$

Fig. 62 describes the strain behavior of the Burger creep phase, for which three different strain responses can be listed:

- 1.a) the instantaneous strain step as the result of the Maxwell spring $\gamma = \tau_0 / G_0$
- 2.a) the gradual increase of the strain curve related to the Kelvin-Voigt element which for t approaching infinity reaches an equilibrium value of τ_0 / G_1
- 3.a) the purely viscous response of the Burger model related to the Maxwell dashpot which is reached after the Kelvin-Voigt element has reached its equilibrium. The slope of the strain-time curve is then constant and is equal to the shear rate $d\gamma/dt = \tau_0 / \eta_0$.

Taking the tangent with this slope $d\gamma/dt = \tau_0 / \eta_0$ and extrapolating it towards the ordinate it will intersect at the “steady-state strain $\gamma_s(0)$ ” which is defined as:

$$\gamma_s(0) = \tau_0 / G_0 + \tau_0 / G_1.$$

i.e. it is equal to the elasticity introduced by the two springs with the moduli G_0 and G_1

When the stress τ_0 is removed the Burger model recovers in a two step manner:

- 1.b) at $t = t_1$ the strain reduces instantaneously by the spring response $\gamma_0 = \tau / G_0$. This is then followed by the two time-functions:

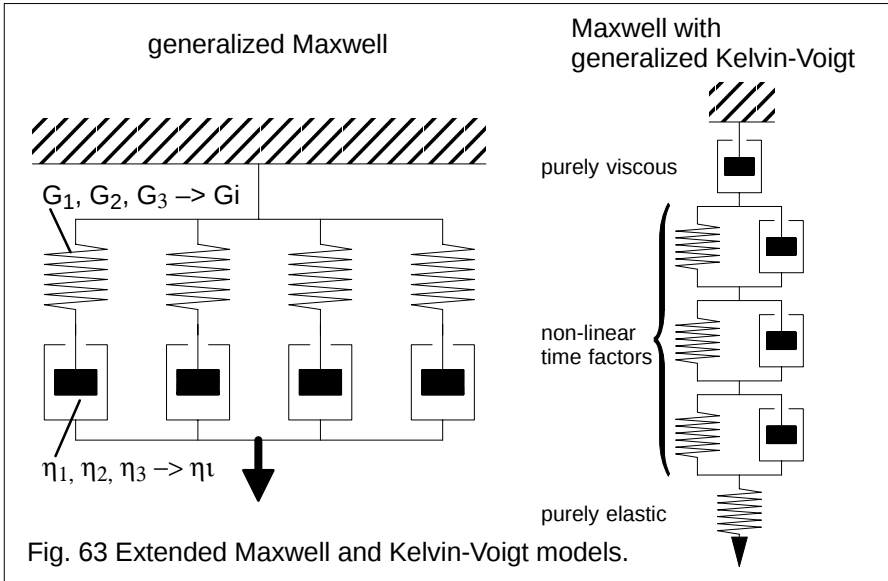
$$\gamma(t) = \tau_0 \cdot t_1 / \eta_0 + \tau_0 / G_1 [e^{-(t-t_1)/\lambda}] \text{ with } t \text{ being longer than } t_1.$$

- 3.b) The term $\tau_0 \cdot t / \eta_0$ is equal to the permanent, non-recovered strain and represents the viscous flow of the Maxwell dashpot.

- 2.b) The other term decreases with an exponential function which for $t = \text{infinity}$ approaches the value τ_0 / G_1 .

If the sample has been tested under conditions within the linear visco-elastic range then the elements that cause an elastic response will give an equal contribution both in the creep and the recovery phase. The retardation times λ in the creep and in the recovery phase are still identical in this model.

c.5.) Extended Maxwell and Kelvin-Voigt models – Fig. 63



Real-life solids and fluids are much more complicated and thus there is a need for more combinations of springs and dashpots to describe their visco-elastic behavior in creep and recovery tests. They can no longer be defined by a single relaxation/retardation time λ but by a relaxation time spectrum with a multitude of λ -values which in their magnitudes are often decades apart. Evaluating the strain recovery curves means to determine the decay of strain – the elastic strain recovery and the permanent strain – viscous flow contribution. Additional information can be found by determining the rates of the strain decay:

Regression calculations may be tried out with 1, 2, 3 or more exponential function elements to find a best-fit equation with the relevant coefficients such as

$$\gamma(t) = a + b \cdot e^{(-t/\lambda_1)} + c \cdot e^{(-t/\lambda_2)} + d \cdot e^{(-t/\lambda_3)} \quad [48]$$

with $a = \tau_0 \cdot t_1/\eta_0$, $b = \tau_0/G_1$, $\lambda_1 =$ retardation time 1, $c = \tau_0/G_2$, $\lambda_2 =$ retardation time 2, etc. – example shown in Fig. 175 on page 289.

In more general terms:
$$\gamma(t) = a + \sum_{i=1}^i [b \cdot e^{(-t/\lambda_i)}] \quad [49]$$

Plotting all the regression curves together with the measured curve will indicate whether the equation with 2 or even 3 terms of this exponential

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function gives a sufficiently good curve-fit and whether one has to deal with two or more retardations times. The other information one gets from the shape of the recovery curve is that especially for high molecular weight polymers retardation times of more than 1000 s can still give a significant contribution to the strain recovery. The conclusion of this recovery behavior is that one has to wait quite a long time in order to substantiate the viscous and the elastic responses of visco-elastic materials.

4.3.3.3 Benefits of creep and the recovery tests.

It is worthwhile to consider how one can make use of creep and recovery tests for testing unknown materials, which are likely to possess visco-elasticity. Evaluation of the strain/time- or the compliance/time curves can lead to the following conclusions:

a.) The strain/time curve slopes continuously upwards and reaches long-term a constant slope of

$$d\gamma/dt = \dot{\gamma} > 0 \rightarrow \text{steady state viscous flow}$$

using:

$$\dot{\gamma} = \tau_0 / \eta_0$$

it can be solved for:

$$\eta_0 = \tau_0 / \dot{\gamma}$$

When testing polymer melts the zero shear viscosity η_0 can give a good insight into their mean molecular weight, inasmuch as η_0 is highly dependent on the weight-average molecular weight M_w and very sensitive to its changes under the condition that M_w is greater than the critical molecular weight M_c :

$$\eta_0 = a M_w^{3.4}$$

a = coefficient

Determining the mean molecular weight of a polymer by means of the creep test is a very rapid method in comparison to other physical methods such as GPC or steady-state-rheometry at extremely low shear rates.

b.) The strain/time- and the compliance curves asymptotically reach a constant level parallel to the abscissa, and during the recovery phase both curves fully return to zero strain and zero compliance: It indicates that the sample is characterized by a yield stress below which the applied stress τ_0 had been assigned. The sample had maintained during the whole test its solid character and all the deformation energy was reversibly stored and fully regained in the recovery phase. This behavior is represented by a Kelvin-Voigt solid.

c.) Most of the time the recovery will lead only to a partial regaining of the initial pre-test shape. Samples are now defined by their viscosity related irreversible-

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loss of deformation energy ($J = t_1/\eta_0$), their elastic recovery of strain (J_s =steady-state compliance) and by their relevant retardation time spectrum.

Whether this property of a sample being partially elastic and partially viscous is positive or detrimental for a product in the manufacturing phase or in its application and usage must be decided by a comparison of these test results with the practical experiences gained in real life. Viscosity and elasticity, which especially in recovery phase can be so clearly distinguished from each other for the given set of test conditions, characterize the rheological behavior of very many fluids of technical and commercial importance. This behavior will relate to the formulation of compounds and mixtures and it will be heavily influenced by production procedures acting on the degree of dispersion of i.e. fillers, the degree of breakup of aggregates etc. Test samples taken during different phases of production, or length of storage, will provide valuable information for the formulating chemist and the quality control supervisor.

d.) Both strain and compliance curves drop to their finite recovery level with a more or less long retardation time. In fact it can be shown for polymers and their blends that this retardation is characterized not just by one but several retardation times $\lambda_1, \lambda_2, \lambda_3$ etc, caused by the retardation times of the different blend components: the relaxation time spectrum. The recovery response of a visco-elastic sample can be described in terms of the compliance as:

$$J(t) = t_1/\eta_0 + \sum_{i=1}^i J_i \cdot e^{-(t-t_1)/\lambda_i} \text{ with } i=1,2,3 \text{ etc.} \quad [50]$$

For $t = \infty$ all e-functions become zero and thus this equation reduces to $J_{(t=\infty)} = t_1/\eta_0$, which equals the permanent strain, i.e. the amount of viscous flow of the sample.

Modern computerization allows one to perform regression calculations with one, two or three e-functions within only some three minutes. For most polymer melts a minimum of three retardations times which differ from each other by a decade are required for a good curve-fit on the recovery curve. Retardation is a very long-term process for high molecular-weight polymers and the time to a full retardation is rarely counted in minutes, more often in hours and sometimes in days. These very long retardation times have important consequences for production processes. They should also be kept in mind when disk-like specimens must be produced for tests in cone-and-plate- or parallel-plate-sensor systems. If the stresses used for the forming of these specimens are not allowed to fully relax prior to the actual tests in the rheometers, one permits significant errors to falsify the expected rheological results.

It is one of the important advantages of these recovery tests that they define the long-term effect of elasticity.

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e.) Extrapolating the tangent of the compliance creep curve when it has reached a constant slope – uniform flow – back to the ordinate will provide an intersect at $J_s(0)$. If the stress applied in the creep phase was within the linear visco-elastic range then this $J_s(0)$ will equal the total elastic recovery in the stress released phase. If the elastic responses in the creep and in the recovery phases are greatly different then one has to assume that the chosen test conditions have been outside the requirements of linear visco-elasticity.

f.) Checking samples for sedimentation, sagging, slumping etc.

Criteria of the quality of paints, creams, ointments or adhesives are that they can resist sedimentation of filler contents, have a long shelf-life, i.e. they do not show a separation of the oil and watery phase, that a coating applied to a vertical wall does not sag and that a thick adhesive layer does not allow slumping. All of these unwanted effects relate to processes at low shear rates which have gravity as the driving force. These processes may be simulated by creep and recovery tests when variable low stresses are applied and the resulting strain is measured. Sedimentation will be prohibited if the sample reaches in the creep phase a constant strain level and therefore exhibits a yield value. Such a sample will fully recover its strain in the second test phase, i.e. no permanent flow is experienced. Testing paints with different levels of stresses will indicate how thick a coat on a vertical wall may be before this coat will start to sag off the wall. On the other hand a paint that resists sagging well will not level well on horizontal surfaces: brush marks may still be seen in “hundreds of years”. The paint rheologist will find creep and recovery tests very useful for finding a proper compromise for the conflicting requirements of a minimum of sagging and a maximum of levelling.

4.3.3.4 Instrumentation for creep and recovery tests.

Considering the responses of model substances to stresses in creep and recovery tests has lead to test methods and suitable instrumentation which will allow a very good insight into the viscous and elastic properties of real visco-elastic solids and fluids. Stresses constant with time but variable in magnitude may be applied either as shear stresses in CS-rotational rheometers such as the HAAKE RheoStress RS100 or as compressional stresses in two-plate-rheometers such as the HAAKE DEFO-Elastometer – Fig. 64.

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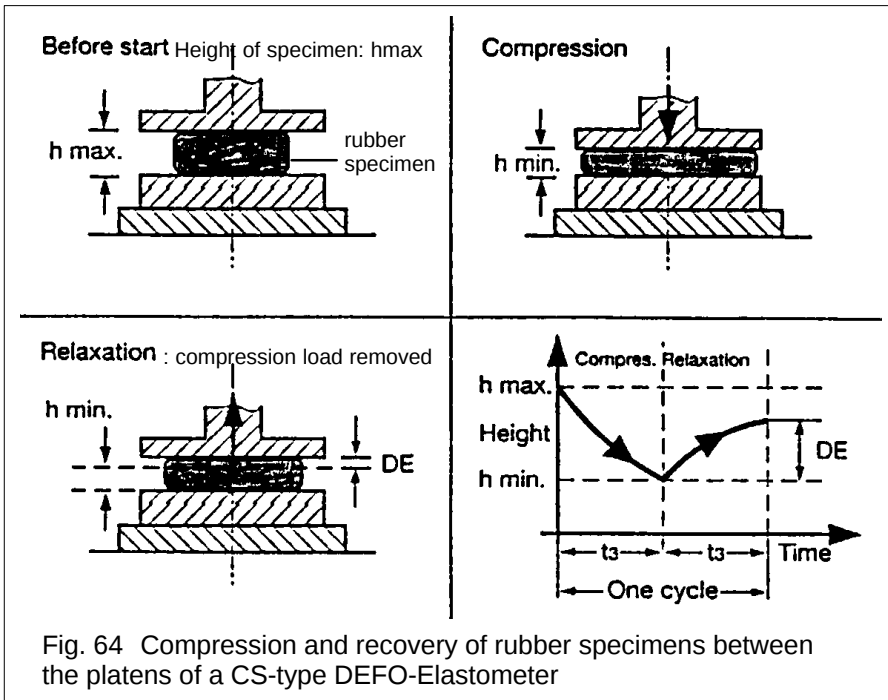


Fig. 64 Compression and recovery of rubber specimens between the platens of a CS-type DEFO-Elastometer

The Defo-Elastometer working also in the CS-mode finds its main application in the testing of raw rubber polymers or rubber compounds, i.e. samples of very high molecular-weight exhibiting high yield values and showing a dominant elastic response to stresses. This instrument applies a defined load/pressure and compresses in a first test phase cylindrical specimens to some 50% of their initial height: $h_{\max}$ to $h_{\min}$. It then allows a retardation – partial recovery DE of the specimen height – during a second load-released test phase.

The Defo-Elastometer with its high percentage of deformation always works in the non-linear visco-elasticity range. While applying compressional loads to cylindrical solid specimens does not provide problems, one would encounter difficulties to provide high shear stresses to similar samples in parallel-plate sensor systems of rotational rheometers without the risk of slippage between the rotating plate and the sample.

To compare different samples on an equal basis of shear history the DEFO-tests require in a first test run to determine the particular load for each polymer which compresses its specimens within a given time span of i.e. 30 s. In the second test run a new specimen is subjected to this load until the height of the specimen has reached the value $h_{\min}$. When at this moment the load is auto-

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matically removed the specimen is free to retard. The recovery versus time is measured for a time period of not less than 10 min. Replotting the retardation values as percentages of the maximum strain and dividing them by the relevant load provides compliance/time curves. They are very valuable to characterize polymers independent of the chosen loads with respect to their viscous and elastic properties.

Testing with the DEFO-Elastometer requires to vacuum-compact polymers such as porous raw rubbers to cylindrical specimens. While this is a “gentle”, slow compaction/deformation at temperatures around 100°C, still good testing requires a sufficient stress release in the specimens during a period of 15 to 30 min.

The RheoStress RS100 is designed to provide an extremely high sensitivity to measure the corresponding deformation even for very small stresses acting on samples of weak visco-elastic structures. In creep and recovery tests it is essential that stressed samples in the second test phase are free to fully recover and reach their true permanent strain level which is indicative of the viscous flow which occurred in the creep phase. It is therefore one of the most important features of such a rheometer that it can make use of an almost friction-free air-bearing for its rotor shaft to prevent that the bearing friction at an almost stand-still of the rotor prohibits or retards the sample retardation.

Similar as for the DEFO-Elastometer one should carefully look into the problem of providing good specimens when using the RS100 with cone-and-plate- or parallel-plate sensor systems for measurements of solids and polymers which are tested as melts:

For proper testing it is strongly advised to preform disk-like specimens to be placed into the gap of cone-and-plate- or parallel-plate sensor systems. Suitable procedures such as moulding under vacuum should be used to ensure that these specimens are homogeneous, are free of pores, meet the space requirements of the shearing gap, and have enough time to fully relax from the stresses that formed the specimens. Of course, one has to ensure that the process of forming these disk-like specimens does not change the polymer chemically before the actual rheological test starts.

4.3.4 Tests with forced oscillation.

4.3.4.1 Description of the test method.

Instead of applying a constant stress leading to a steady-state flow, it has become very popular to subject visco-elastic samples to oscillating stresses or oscillating strains. In a rheometer such as the RheoStress100 in the CS-mode, the stress may be applied as a sinusoidal time function:

$$\tau = \tau_0 \cdot \sin(\omega \cdot t) \quad [51]$$

The rheometer then measures the resulting time-dependent strain. Tests with oscillating stresses are often named “dynamic tests”. They provide a different

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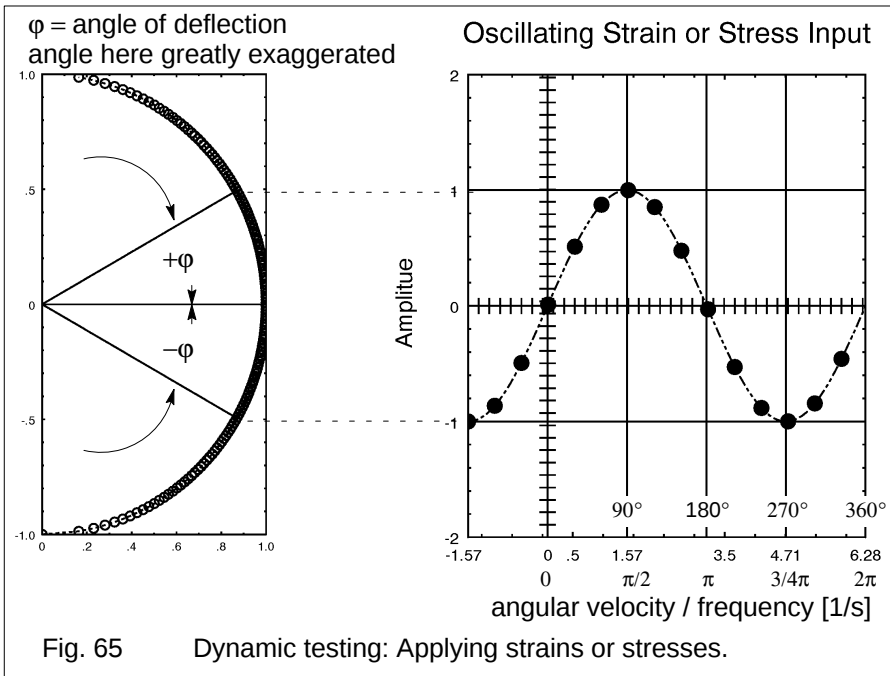
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approach for the measurement of visco-elasticity in comparison to the creep and recovery tests. Both tests complement each other since some aspects of visco-elasticity are better described by the dynamic tests and others by creep and recovery.

Dynamic tests provide data on viscosity and elasticity related to the frequency applied: this test mode relates the assigned angular velocity or frequency to the resulting oscillating stress or strain. Inasmuch as normal tests not only require testing at one particular frequency but a wide range of frequencies, the whole test is often quite time consuming.

While measuring the dynamic viscosity of a Newtonian liquid in steady-state, rotational flow – after a defined temperature level has been reached – will take only a minute or two, measuring the visco-elasticity of i.e. a polymer can easily require a test period more than 10-times longer in dynamic testing – and in creep and recovery as well!

Please note: When working in the linear visco-elastic region dynamic tests can be run in the CS- or the CR-rheometer-mode giving identical results. For simplifying mathematical reasons only, the explanation to be given uses the CR-concept.



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Running an oscillatory test with a rotational rheometer means that the rotor – either the upper plate or the cone – is no longer turning continuously in one direction but it is made to deflect with a sinusoidal time-function alternatively for a small angle ϕ to the left and to the right. The sample placed into that shearing gap is thus forced to strain in a similar sinusoidal function causing resisting stresses in the sample. Those stresses follow again a sinusoidal pattern, the amplitude and the phase shift angle δ of which is related to the nature of the test sample.

To stay within the realm of linear visco-elasticity, the angle of deflection of the rotor is almost always very small: often not more than 1° .

Please note: the angle ϕ as shown in the schematic of Fig. 65 is for explanation reasons much enlarged with respect to reality.

This leads to a very important conclusion for the dynamic tests and the scope of their application: samples of visco-elastic fluids and even of solids will not be mechanically disturbed nor will their internal structure be ruptured during such a dynamic test. Samples are just probed rheologically for their “at-rest structure”.

4.3.4.2 Some theoretical aspects of dynamic testing.

In order to give some basic background for the interpretation of dynamic test data a more theoretical discussion using the spring/dashpot-models is inserted, which may be omitted by less theoretically-minded readers: pages 114 to 124.

It has been already shown that springs representing an elastic response are defined by: $\tau = G \cdot \gamma$.

Dashpots represent the response of a Newtonian liquid and are defined by:

$$\tau = \eta \cdot \dot{\gamma}$$

These basic rheological elements and their different combinations are discussed this time with respect to dynamic testing:

a.) The spring model – Fig.66

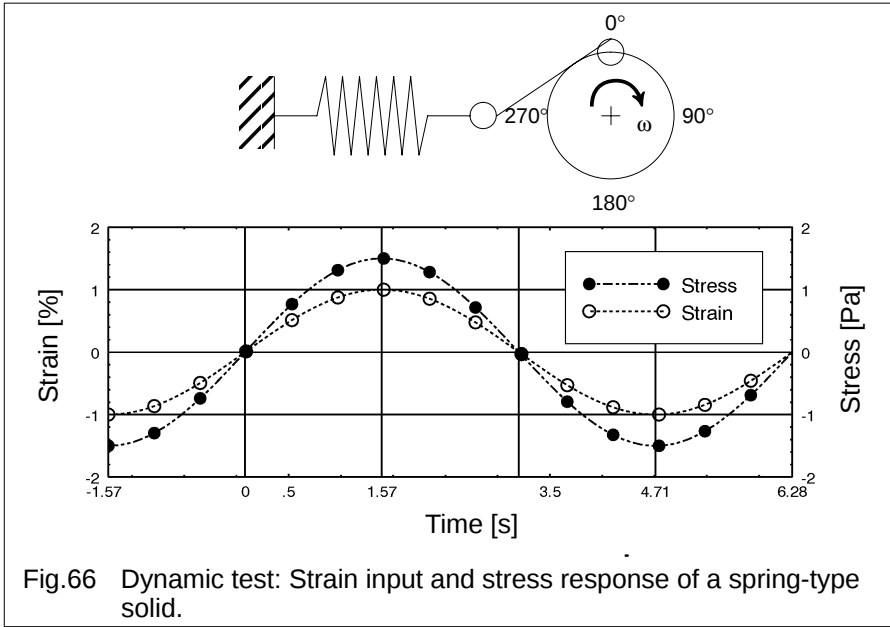


Fig.66 Dynamic test: Strain input and stress response of a spring-type solid.

This schematic indicates how a spring may be subjected to an oscillating strain when the pivoted end of a crankshaft is rotated a full circle and its other end compresses and stretches a spring. If the angular velocity is ω and γ_0 is the maximum strain exerted on the spring then the strain as a function of time can be written:

$$\gamma = \gamma_0 \cdot \sin(\omega \cdot t) \quad [52]$$

this leads to the stress function:

$$\tau = G \cdot \gamma_0 \cdot \sin(\omega \cdot t) \quad [53]$$

The diagram indicates that for this model strain and stress are in-phase with each other: when the strain is at its maximum, this is also true for the resulting stress.

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b.) The dashpot model – Fig. 67

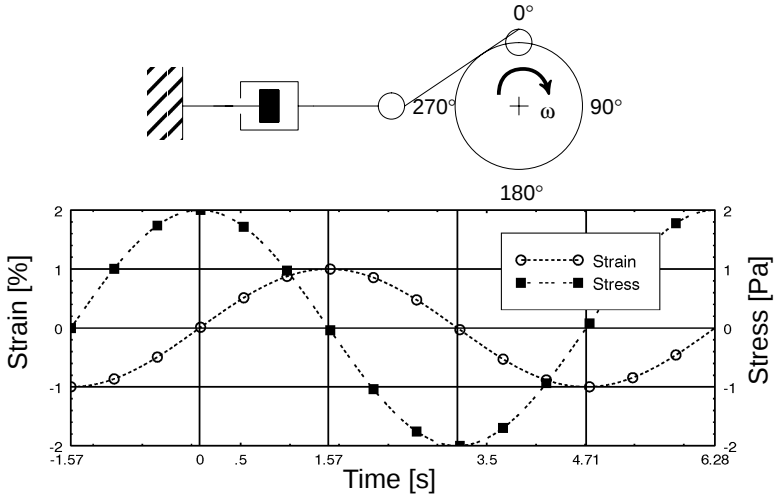


Fig.67 Dynamic test: Strain input and stress response of a Newtonian liquid or a dashpot

If the spring is exchanged by a dashpot and the piston is subjected to a similar crankshaft action, the following equations apply:

$$\dot{\gamma} = d \gamma / dt = \omega \cdot \dot{\gamma} \cdot \cos(\omega \cdot t) \quad [54]$$

Substituting this into the dashpot equation:

$$\tau = \eta \cdot d \gamma / dt = \eta \cdot \omega \cdot \gamma_0 \cdot \cos(\omega \cdot t) \quad [55]$$

It is evident also in Fig.67 that for the dashpot the response of τ is 90° out-of-phase to the strain. This can also be expressed by defining a phase shift angle $\delta = 90^\circ$ by which the assigned strain is trailing the measured stress.

The above equation can then be rewritten:

$$\tau = \eta \cdot \omega \cdot \gamma_0 \cdot \cos(\omega \cdot t) = \eta \cdot \omega \cdot \gamma_0 \cdot \sin(\omega \cdot t + \delta) \quad [56]$$

Whenever the strain in a dashpot is at its maximum, the rate of change of the strain is zero ($\dot{\gamma} = 0$). Whenever the strain changes from positive values to negative ones and then passes through zero, the rate of strain change is highest and this leads to the maximum resulting stress.

An in-phase stress response to an applied strain is called “elastic”.

An 90° out-of-phase stress response is called “viscous”.

If a phase shift angle is within the limits of $0 < \delta < 90^\circ$ is called “visco-elastic”.

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c.) The Kelvin-Voigt model. (triangle data points) – Fig. 68

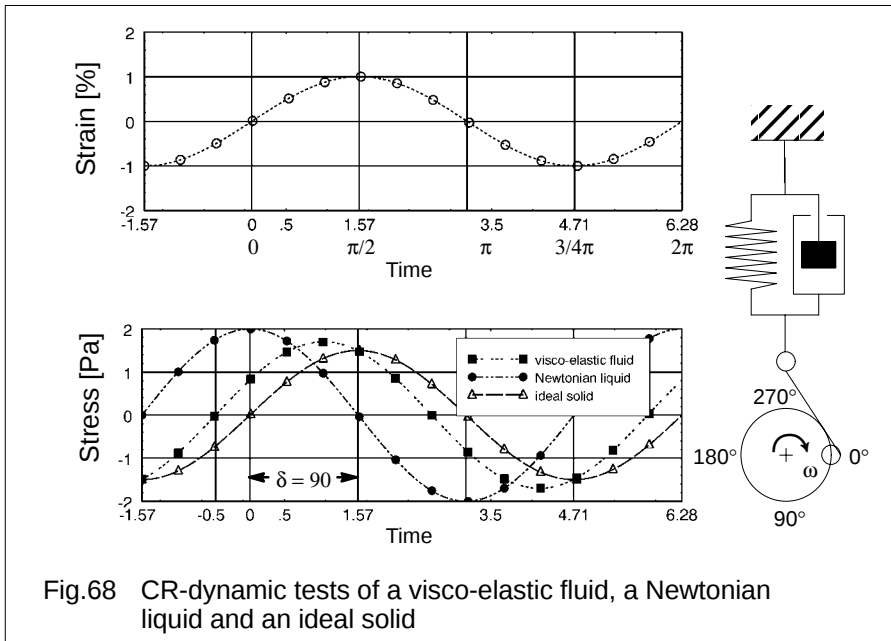


Fig.68 CR-dynamic tests of a visco-elastic fluid, a Newtonian liquid and an ideal solid

As previously explained, this model combines a dashpot and spring in parallel. The total stress is the sum of the stresses of both elements, while the strains are equal.

Its equation of state is:

$$\tau = G \cdot \gamma + \eta \cdot d\gamma/dt \quad [57]$$

Introducing the sinusoidal strain this leads to:

$$\tau = G \gamma_0 \sin(\omega \cdot t) + \eta \cdot \omega \cdot \gamma_0 \cos(\omega \cdot t) \quad [58]$$

The stress response in this two-element-model is given by two elements being elastic $\rightarrow \delta = 0$ – and being viscous $\rightarrow \delta = 90^\circ$.

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d.) the Maxwell model. (black dot data points) – Fig. 69

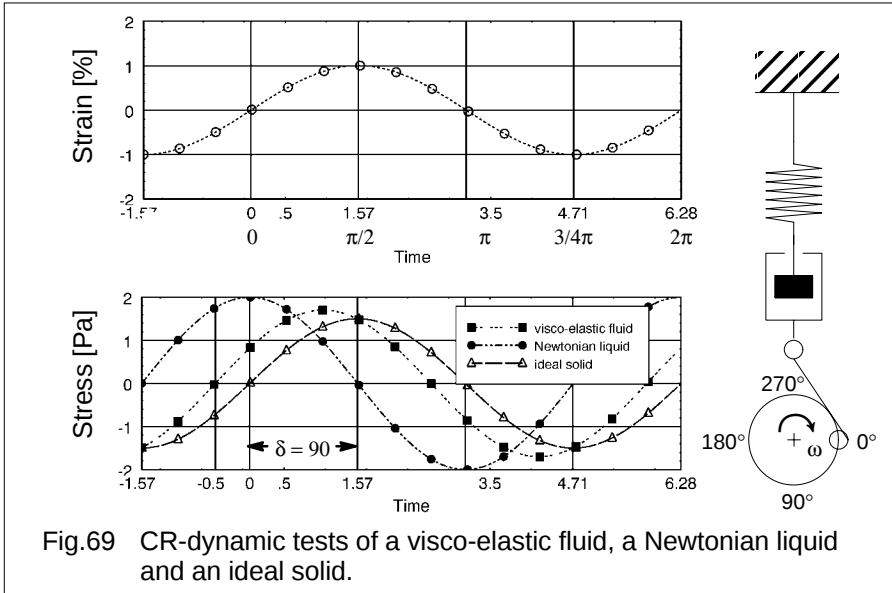


Fig.69 CR-dynamic tests of a visco-elastic fluid, a Newtonian liquid and an ideal solid.

This model combines a dashpot and a spring in series for which the total stress and the stresses in each element are equal and the total strain is the sum of the strains in both the dashpot and the spring.

The equation of state for the model is:

$$1/G \cdot (d\tau/dt) + \tau/\eta = d\gamma/dt \quad [59]$$

Introducing the sinusoidal strain function

$$1/G \cdot (d\tau/dt) + \tau/\eta = \omega \cdot \gamma_0 \cdot \cos(\omega \cdot t)$$

This differential equation can be solved:

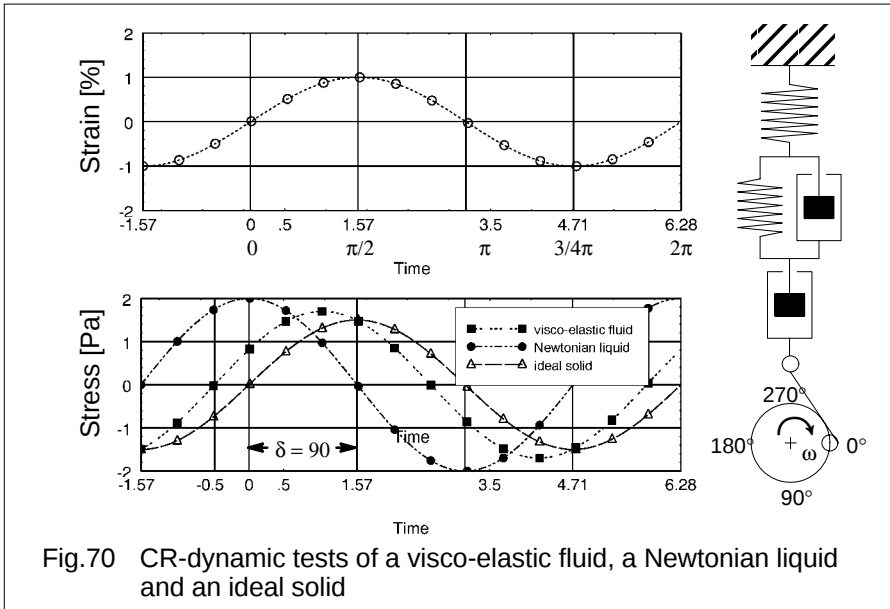
$$\tau = [G \cdot \lambda^2 \cdot \omega^2 / (1 + \lambda^2 \cdot \omega^2)] \cdot \sin(\omega \cdot t) + [G \cdot \lambda \cdot \omega / (1 + \lambda^2 \cdot \omega^2)] \cdot \cos(\omega \cdot t) \quad [60]$$

In this equation the term $\lambda = \eta/G$ stands for the relaxation time. As in the Kelvin-Voigt model the stress response to the sinusoidal strain consists of two parts which contribute the elastic sin-wave function with $\varphi = 0^\circ$ and the viscous cosin-wave-function with $\varphi = 90^\circ$.

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e.) Testing of real visco-elastic samples. (black square data points) – Fig.70



Real visco-elastic samples are more complex than either the Kelvin-Voigt solid or the Maxwell liquid. Their phase shift angle is positioned between $0 < \delta < 90^\circ$. G^* and δ are again frequency dependent:

In a CR-test-mode the strain is assigned with an amplitude γ_0 and an angular velocity ω as:

$$\gamma = \gamma_0 \cdot \sin(\omega \cdot t)$$

The resulting stress is measured with the stress amplitude τ_0 and the phase angle δ :

$$\tau = \tau_0 \cdot \sin(\omega \cdot t + \delta)$$

The angular velocity is linked to the frequency of oscillation by:

$$\omega = 2\pi \cdot f$$

The frequency f is given in units of Hz = cycles/s

the dimension of ω is either: 1/s or rad/s.

ω multiplied by time t defines the angular deflection in radians:

$2 \cdot \pi$ corresponds to a full circle of 360° .

It is common to introduce the term “complex modulus G^* ” which is defined as:

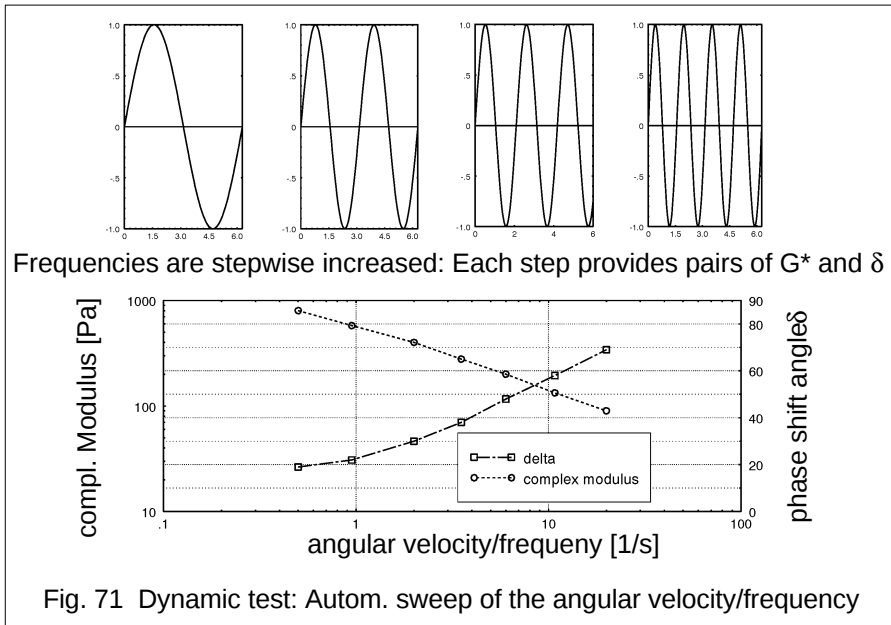
$$|G^*| = \tau_0 / \gamma_0$$

G^* represents the total resistance of a substance against the applied strain.

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It is important to note that for real visco-elastic materials both the complex modulus and the phase angle δ are frequency dependent. Therefore normal tests require one to sweep an assigned frequency range and plot the measured values of G^* and δ as a function of frequency. A frequency sweep means: the strain frequency is stepwise increased and at any frequency step the two resulting values of G^* and δ are measured.



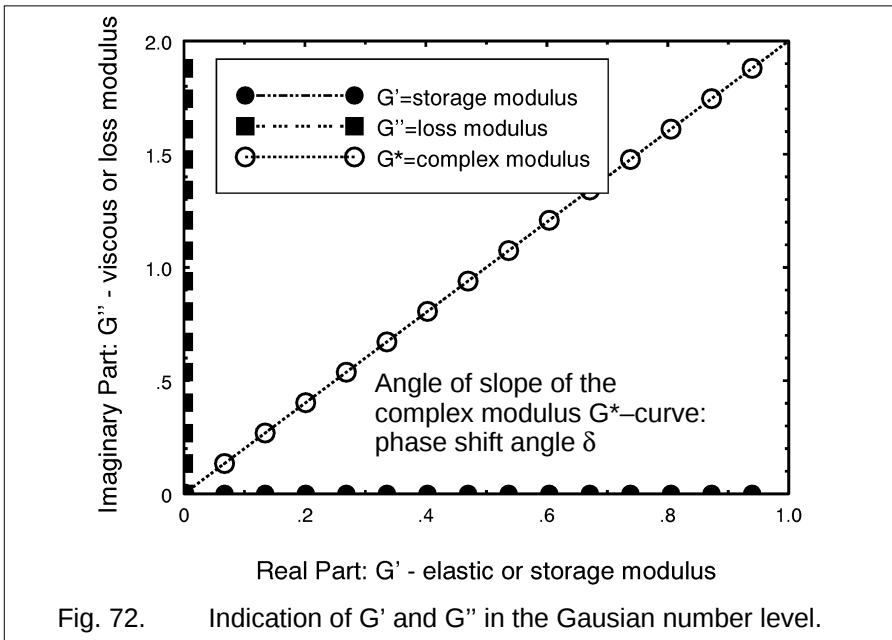
Sweeping the frequency within a given range will provide the graphs of G^* and δ . A decline of a δ /frequency-curve within its full range from 0 to 90° marks a increase of the viscous and the corresponding decrease of the elastic behavior of a sample tested. The assigned strain wave – in the CS-mode: the stress wave – is defined by up to 150 data points. This leads to corresponding 150 stress values forming a sinusoidal wave differing to the strain wave with respect to the amplitude and the angle δ . The method of a “cross-correlation of harmonic signals” performed by the computer software determines for the “input” of γ_0 and $\omega \cdot t$ the “output” of G^* and δ . Since it always requires at least a single full cycle or two to reach an equilibrium for any new frequency value, the computer software normally takes 3 cycles of the assigned wave to get significant G^* and δ -values. For small values of frequency of i.e. $\omega = 0.001$ 1/s this then means that it takes 1000 seconds (about 16 min) to measure a single pair of G^* - and δ -values from one cycle or more than 3/4 hour from 3 cycles. For time economy reasons, tests are rarely run at frequencies below 0.01 1/s.

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These data must still be transformed into the viscous and the elastic components of the visco-elastic behavior of the sample. This is best done by means of an evaluation method often used in mathematics and physics:

f.) The Gaussian number level for an easy distinction between the viscous and elastic behavior of samples subjected to dynamic tests.



The Gaussian number level makes use of complex numbers, which allow working with the root of the negative number

$$\sqrt{-1} = i$$

Complex numbers can be shown as vectors in the Gaussian number level with its real and its imaginary axes.

The complex modulus G^* can be defined as:

$$G^* = G' + i G'' = \tau_0(t)/\gamma_E(t) \quad [61]$$

In this equation are:

$$G' = G^* \cos \delta = \tau_0/\gamma_0 \cdot \cos \delta = \text{elastic or storage modulus}$$

$$G'' = G^* \sin \delta = \tau_0/\gamma_0 \cdot \sin \delta = \text{viscous or loss modulus}$$

The term “storage” modulus G' indicates that the stress energy is temporarily stored during the test but that it can be recovered afterwards. The term “loss

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modulus G'' hints at the fact that the energy which has been used to initiate flow is irreversibly lost having been transformed into shear heat.

If a substance is purely viscous then the phase shift angle δ is 90° :

$$G' = 0 \text{ and } G'' = G^*$$

If the substance is purely elastic then the phase shift angle δ is zero:

$$G' = G^* \text{ and } G'' = 0$$

Alternatively to the complex modulus G^* one can define a complex viscosity η^* :

$$\eta^* = G^*/i\omega = \tau_0/(\gamma_0 \cdot \omega) \quad [62]$$

It describes the total resistance to a dynamic shear. It can again be broken into the two components of the storage viscosity η'' – the elastic component – and the dynamic viscosity η' – the viscous component.

$$\begin{aligned} \eta' &= G''/\omega = [\tau_0/(\gamma_0 \cdot \omega)] \cdot \sin \delta \\ \eta'' &= G'/\omega = (\tau_0/(\gamma_0 \cdot \omega)) \cdot \cos \delta \end{aligned}$$

It is also useful to define again as in 4.3.3 the term of the complex compliance J^* with its real and the imaginary components:

$$J^* = 1/G^* = J' + i \cdot J'' \quad [63]$$

The stress response in dynamic testing can now be written either in terms of moduli or of viscosities:

$$\begin{aligned} \tau(t) &= G' \cdot \gamma_0 \cdot \sin(\omega \cdot t) + G'' \cdot \gamma_0 \cdot \cos(\omega \cdot t) \\ \tau(t) &= \eta'' \cdot \gamma_0 \cdot \omega \cdot \sin(\omega \cdot t) + \eta' \cdot \gamma_0 \cdot \omega \cdot \cos(\omega \cdot t) \end{aligned}$$

Modern software evaluation allows one to convert G^* and δ into the corresponding real and imaginary components G' and G'' , η' and η'' or J' and J'' . Sweeping the frequency range then allows to plot the curves of moduli, viscosities and compliances as a function of frequency.

g.) The dependency of the dynamic data on the angular velocity.

Real substances are neither Voigt-solids nor Maxwell-liquids but are complex combinations of these basic models. In order to grade the dynamic data of real substances it is useful to see how the two basic models perform as a function of angular velocity.

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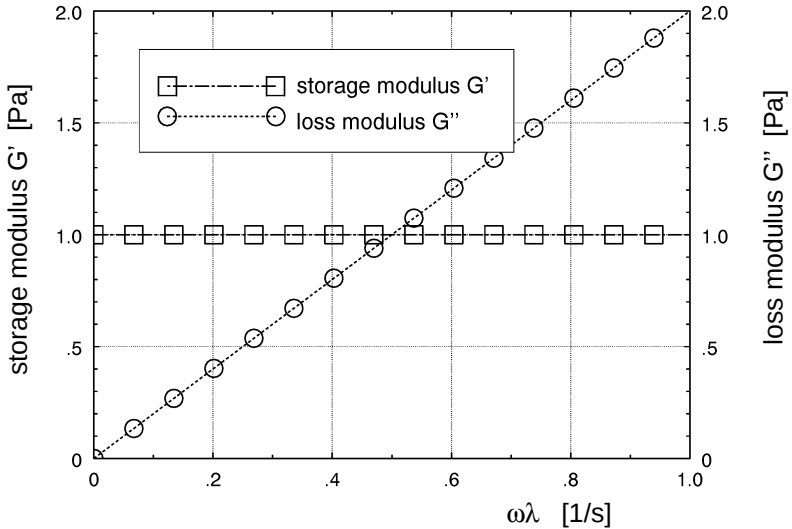


Fig. 73 Dynamic test of a Voigt solid

In a dynamic test of a Voigt solid the moduli are expressed as: G' is directly linked to the spring modulus G , while $G'' = \eta \cdot \omega$ – Fig. 73.

This indicates that G' is independent of the frequency while G'' is linearly proportional to the frequency. At low frequencies this model substance is defined by its spring behavior, i.e. the viscous component G'' exceeds the elastic component G' . At an intermediate frequency value both components are equal and for high frequencies the elastic component becomes dominant.

Making use of:

$$\lambda = \eta/G$$

the above equation becomes: $G'' = G \cdot \omega \cdot \lambda$

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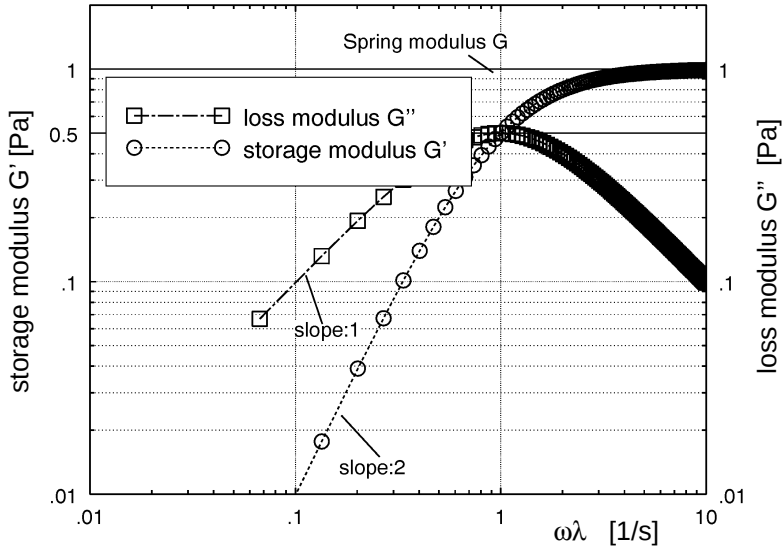


Fig. 74 Dynamic test of a Maxwell fluid

In a dynamic test of a Maxwell fluid the moduli as a function of $\omega\lambda$ are:

$$G' = G \cdot \omega^2 \cdot \lambda^2 / [1 + (\omega^2 \cdot \lambda^2)] \quad [64]$$

$$G'' = G \cdot \omega \cdot \lambda / [1 + (\omega^2 \cdot \lambda^2)] \quad [65]$$

When the term $(\omega\lambda)$ becomes very small and one uses the term $\lambda = \eta/G$ (dashpot viscosity η / spring modulus G) then

$$G' = G \cdot \lambda^2 \cdot \omega^2 \text{ and } G'' = G \cdot \omega \cdot \lambda = \eta \cdot \omega$$

When this term $(\omega\lambda)$ becomes very high then

$$G' = G \text{ and } G'' = G/(\lambda \cdot \omega) = G^2/(\eta \cdot \omega)$$

At low frequency values the viscous component G'' is larger than the elastic component G' . The Maxwell model reacts just as a Newtonian liquid, since the dashpot response allows enough time to react to a given strain. At high frequencies the position of G' and G'' is reversed: The model liquid just reacts as a single spring since there is not sufficient time for the dashpot to react in line with the assigned strain.

This behavior is shown in Fig. 74. Its schematic diagram with double logarithmic scaling plots the two moduli as a function of $(\omega\lambda)$. At low values of frequency the storage modulus G' increases with a slope of $\tan \alpha = 2$ to reach asymptotically the value of the spring modulus G at a high frequency. The loss

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modulus G' increases first with the slope $\tan \alpha = 1$, reaches a maximum at $\omega \cdot \lambda = 1$, and drops again with the slope of $\tan \alpha = -1$. At $\omega \cdot \lambda = 1$ both moduli are equal.

For the evaluation of dynamic test results it is of interest to see at what level of frequency the curves of the two moduli intersect and what their slopes are, especially at low frequencies.

For very low values of angular velocity/frequency one can evaluate from the value of G'' the dynamic dashpot viscosity $\eta_N = \eta_0 = G''/\omega$ and the relaxation time $\lambda = G''/(G'' \cdot \omega)$.

h.) Cox-Merz Relation.

Empirically the two scientists who gave this relation their name found that the steady-shear viscosity measured as function of shear rate could be directly compared to the dynamic complex viscosity measured as a function of angular velocity:

$$\eta(\dot{\gamma}) = \eta^*(\omega) \rightarrow \dot{\gamma} \approx \omega$$

This relationship was found to be valid for many polymer melts and polymer solutions, but it rarely gives reasonable results for suspensions.

The advantage of this Cox-Merz Relation is that it is technically simpler to work with frequencies than with shear rates. Polymer melts and solutions cannot be measured at shear rates most of time not higher than 50 1/s in a rotational rheometer in open sensor systems such as "cone/plate" or "plate/plate" due to the elastic effects encountered – Weissenberg effect. Thus instead of measuring a flow curve in steady-state shear, one can more easily use the complex viscosity of dynamic testing.

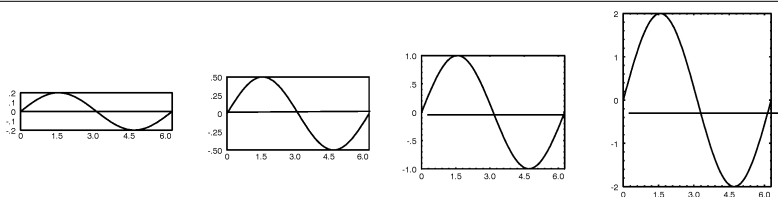
i.) The determination of the linear visco-elastic range.

In the chapter describing the relevance of creep and recovery tests the importance of testing within the linear visco-elastic range was demonstrated. This range has also great importance for the dynamic testing. To determine the limit between the linear- and the non-linear visco-elastic range one can run a single simple test:

Instead of performing dynamic tests with a fixed stress or strain amplitude and perform a frequency sweep, another test can be run with a fixed frequency of e.g. 1 Hz while an amplitude sweep is performed. The amplitude is automatically increased stepwise, whenever sufficient data for the strain/stress correlation have been acquired. Results of such a test are plotted as G^* versus amplitude.

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Stepwise increase of the stress amplitude

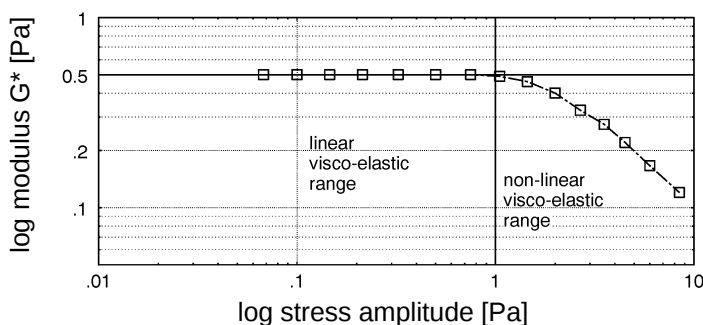


Fig. 75 Dynamic test: Change of G^* in a stress amplitude sweep

In this schematic diagram – Fig. 75 – the complex modulus G^* curve runs parallel to the abscissa until at $\tau_0 = 1$ Pa this curve starts to break away in this example from the constant level of $G^* = 0.5$ Pa.

The linear visco-elastic range is limited to that amplitude range for which G^* is constant. In the theory of linear visco-elasticity the relevant equations are linear differential equations and the coefficients of the time differentials are constants, i.e. are material constants. Leaving this linear visco-elastic range by selecting higher amplitudes and consequently higher stresses means non-accountable deviations for the measured data of the materials tested linked to the chosen test parameters and the instrumentation used: under these conditions the sample is deformed to the point that the internal temporary bonds of molecules or of aggregates are destroyed, shear-thinning takes place and a major part of the introduced energy is irreversibly lost as heat.

Important to note:

The consequence of the importance of linear visco-elasticity is that any dynamic tests for unknown samples must start with a stress amplitude sweep.

Having determined the amplitude that keeps tests of a particular sample safely within the linear visco-elastic region, one can then proceed with further tests using the frequency sweep to measure the sample's visco-elastic behavior.

Samples subjected to production conditions are most of the time subjected to high shear deformation conditions which are linked to the non-linear visco-elastic behavior of these materials. It may then make good sense to measure both the data of linear and of non-linear visco-elasticity for a relative comparison of samples with respect to their processibility.

4.3.4.3 Benefits of dynamic testing.

a.) Insight into the molecular structure of thermoplastic polymer melts.

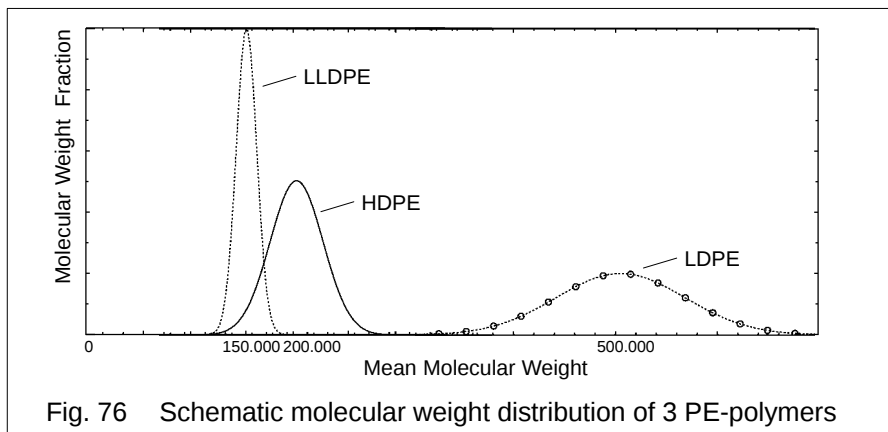


Fig. 76 Schematic molecular weight distribution of 3 PE-polymers

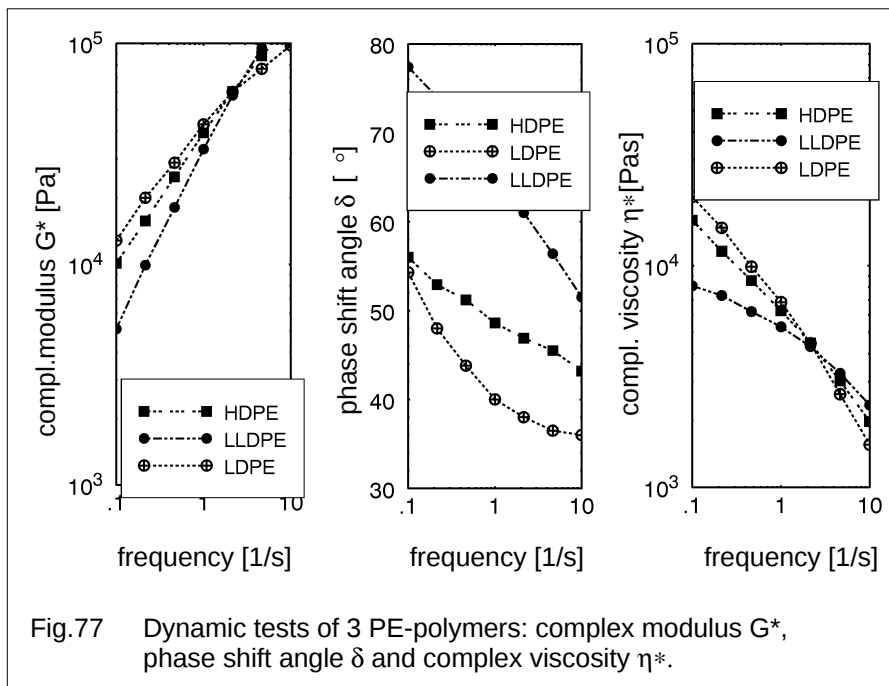
These melts may differ in their mean molecular-weight and in their molecular-weight distribution as indicated for three types of polyethylenes in Fig. 76. High molecular-weight polymers are additionally influenced by their degree of long chain branching which is a decisive factor in the ease of these polymers with respect to their processibility. The latter term is strongly related to the rheological behaviour of these melts and one can expect some correlation between rheological test data and the structural elements of individual molecules and the interaction of billions of them in any volume element of a melt. All three polyethylenes were tested in a parallel-plate sensor system of a CS-rheometer in a dynamic test mode covering an angular speed – frequency – range of 0.1 to 10 at a test temperature of 200°C.

Polymer LDPE defined by the highest mean molecular-weight but also by its very wide molecular-weight distribution, especially in comparison to Polymer LLDPE which possesses a much lower mean molecular-weight combined with a narrow molecular-weight distribution. LDPE may be considered a blend containing quite a reasonable percentage of both very high molecular-weight and very low molecular-weight molecules. The latter may act as some kind of low viscosity lubricants for the rest of the polymer while the former may show up as an additional elasticity parameter. Dynamically tested one can assume

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that these percentages in the LDPE will have some strong influence on this polymer response in comparison to the one of the LLDPE with its more uniform molecular structure.



In Fig. 77 the complex modulus, the phase shift angle and the complex viscosity are plotted as a function of the given range of the frequency.

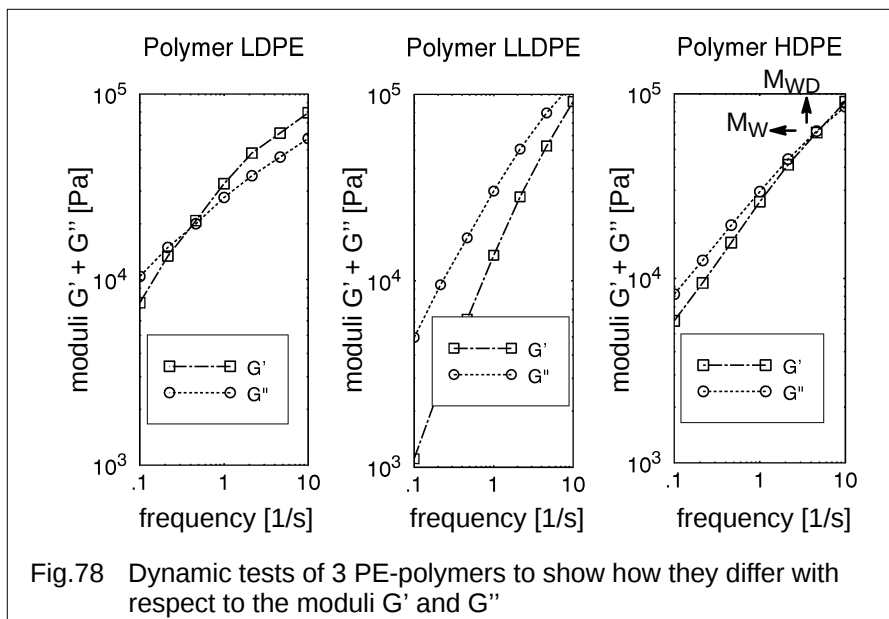
LDPE and LLDPE clearly differ: ∅

a1.) both the complex moduli- and the complex-viscosity curves are crossing with respect to the frequency, i.e. at low frequency the LLDPE shows a lower modulus and lower viscosity than the LDPE but at high frequency the polymers change their positions.

a2.) both polymers show a decrease of the phase shift angle δ with frequency, i.e. they change from a more viscous to a more elastic response, but the LLDPE starts at low frequency at a much more viscous level than the LDPE.

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In Fig.78 the emphasis is laid on the correlation of the G' - and G'' - functions with respect to the frequency: Comparing the LLDPE- and the LDPE diagrams one will notice that their cross-over points of the G' - and the G'' - curves differ by 2 decades of frequency. Already at a frequency of less than 1 Hz the LDPE becomes more elastic than viscous, while the LLDPE is still more viscous than elastic at frequencies below some 50 Hz.

The HDPE is taking a middle position as one can also see in Fig. 77. In comparing similar polymer melts of the same polymer family by means of dynamic tests one will find the following tendencies: increasing the mean molecular weight M_W moves the cross-over point of the G'/G'' -curves to lower frequencies and decreasing the molecular weight distribution M_{WD} moves the cross-over point to higher values of the moduli. These phenomena are also marked in the upper right hand corner of HDPE diagram of Fig.78.

Test results as the ones above indicate that differences in the molecular structure of polymers can be “fingerprinted” in the frequency dependence of the moduli, the phase shift angle and the complex viscosity data. These data as such get their scientific value by the comparison with data measured for polymers of well defined structures.

Having thus “scaled” test results with standard polymers one can use the dynamic results determined in quality control of to grade polymers and then

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link any data variation with e.g. an increased molecular weight distribution or the percentage of long-chain branching.

b.) Differentiation between thermoplastic polymer melts and polymers with a crosslinked molecular structure as indicated by dynamic tests.

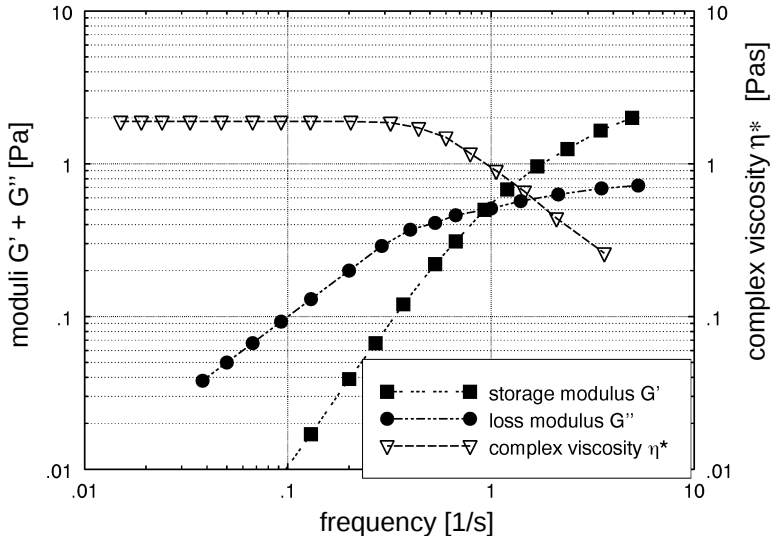


Fig. 79 Dynamic test of a thermoplastic melt: moduli G' , G'' and the complex viscosity η^* .

Non-crosslinked thermoplastic polymer melts – Fig. 79 – show an elastic response and some viscous flow when subjected to sinusoidal stresses. At low angular velocities the G'' -curve slopes upwards with a slope of $\tan \alpha = 1$ while the slope of the storage modulus is $\tan \alpha = 2$. At low values of ω the G'' -curve is well above the G' -curve. The two curves of the moduli cross-over at a particular value of the angular velocity which is characteristic for the polymer structure. For even higher angular speeds the elastic response indicated by G' exceeds the viscous one of G'' . The viscosity curve shows a “Newtonian range” at low frequencies and then starts to decrease: the complex viscosity shows a very similar behavior to the dynamic viscosity of steady-state flow which also shows shear-thinning at higher shear rates.

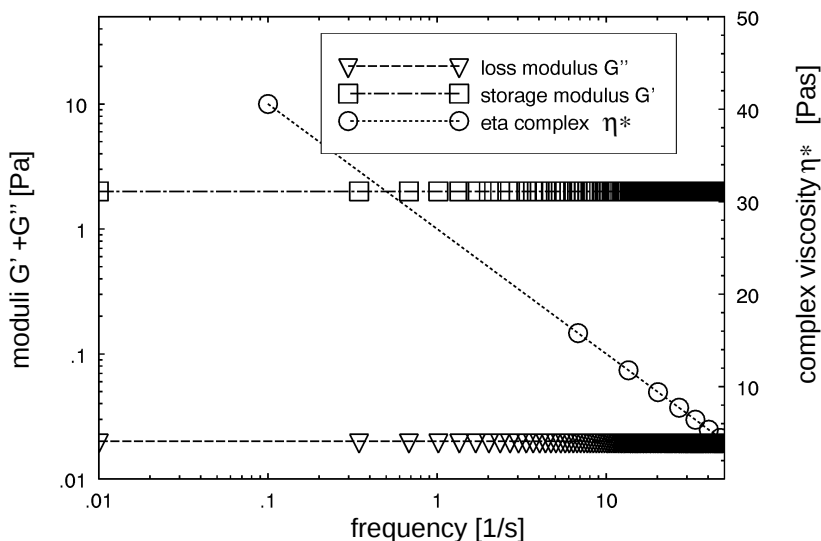


Fig. 80 Dynamic tests of a fully crosslinked polymer

When thermosetting polymers or rubber compounds – Fig.80 – which can be chemically crosslinked, have become fully hardened or vulcanized they turn into a solid, i.e. their volume elements when stressed can no longer irreversibly change places – unless the mass is ground to powder and is thus destroyed. The exponent of the “power law” (Ostward de Waele equation) changes as the result of this crosslinking process from e.g. $n = 1/2$ to $n = 0$, which means that in double logarithmic scaling of the viscosity plot versus angular velocity the viscosity curve is a straight line with a slope of $\tan \alpha = -1$. The position of the moduli with respect to each other also changes: The G' -curve becomes a straight line parallel to the ω -abscissa well above the G'' -curve. These two curves no longer cross-over. The moduli of the cured material are thus independent of the angular velocity and the elastic response to stresses greatly surpasses the viscous one. The level of the G' -curve is said to coincide with the number of crosslinks along the original chain molecules.

c.) Monitoring the crosslinking process of thermosetting polymers by dynamic tests.

Rheometer tests in the CS-mode provide a very simple and informative test method to follow the process of crosslinking the polymer molecules. A comparison to other cure tests with continuously rotating rotors of laboratory-size internal mixers surrounded by the hardening polymer within the mixing chamber is worthwhile: Such a test shows during curing an overlapping of two

conflicting processes before the mass is fully cured: the viscosity increase due to the chemical curing and the mechanical destruction of the mass by means of the rotating rotors which finally grind the mass to some kind of no longer fusible powder. The dynamic cure test is non-destructive for the thermosetting polymer and the molecules are free to crosslink up to the fully cured stage if enough testing time is allowed. Using parallel-plate sensor systems has the additional advantage of the relative ease of removing the cured disk-like sample from the sensor system. Only a few cm^3 of sample volume are required if the gap sizes between the plates are set to only a millimeter or two. The rate of heating the sample to the test temperature is short and a constant temperature level is easily maintained for the length of the test period.

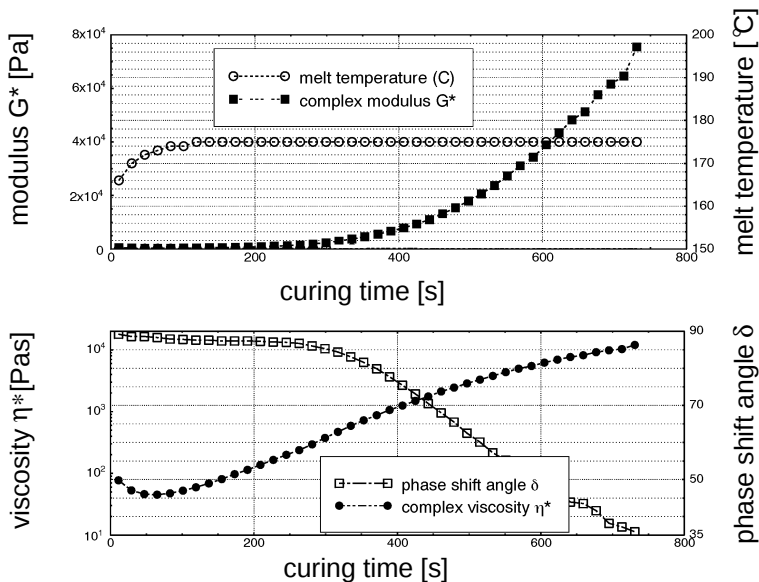


Fig. 81 Dynamic testing of a thermosetting polymer

Fig. 81 indicates in the upper diagram both the sample temperature and the complex modulus as a function of time. G^* increases as the result of the hardening process. This can also be seen in the lower diagram: the phase shift angle δ decreases from $\delta = 90^{\circ} \rightarrow$ fully viscous to a $\delta < 35^{\circ}$. This angle had not reached the lowest level possible ($\delta = 0 \rightarrow$ fully cured) when this test had been terminated. The complex viscosity initially shows a decrease related to the melt temperature increase but then the viscosity increases as expected.

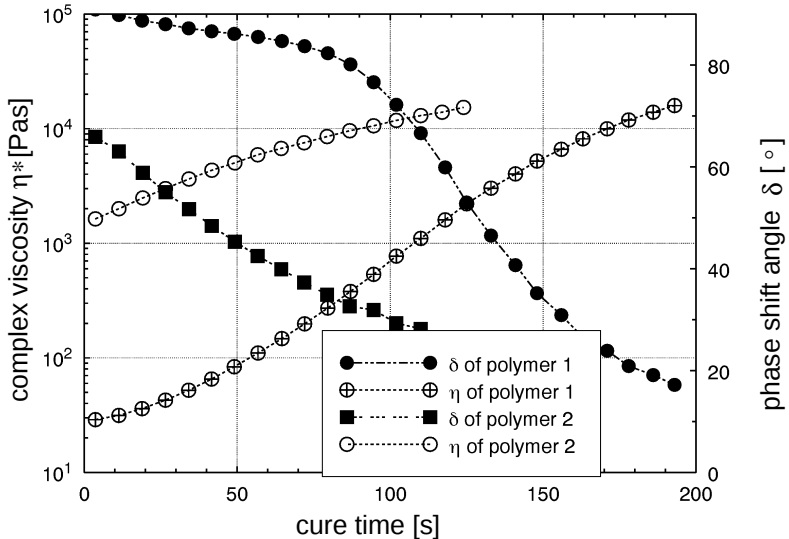


Fig. 82 Dynamic test: Curing of 2 thermosets

Fig.82 provides a comparison of two thermosetting resins, which show marked differences in their curing rates with respect to the complex viscosity η^* and the phase angle δ .

d.) Monitoring the recovery of thixotropic gel structures after that structure has been destroyed by a pre-shear phase.

As mentioned in chapter 9.1 thixotropic samples have a weak structure, which as the result of constant or dynamic shear may be temporarily destroyed resulting in a viscosity drop with time. It is characteristic for these thixotropic samples such as paints, bubble soaps, jellies, or ketchup that they can recover their original gel structure when left at rest for some time. The rebuilding of this structure and the increase of viscosity is very time-dependent. For many technical applications such as for paints the rate of the structure regeneration is very important, because the paint may have already sagged off vertical walls long before the applied coat of paint had sufficiently rethickened to prevent sagging.

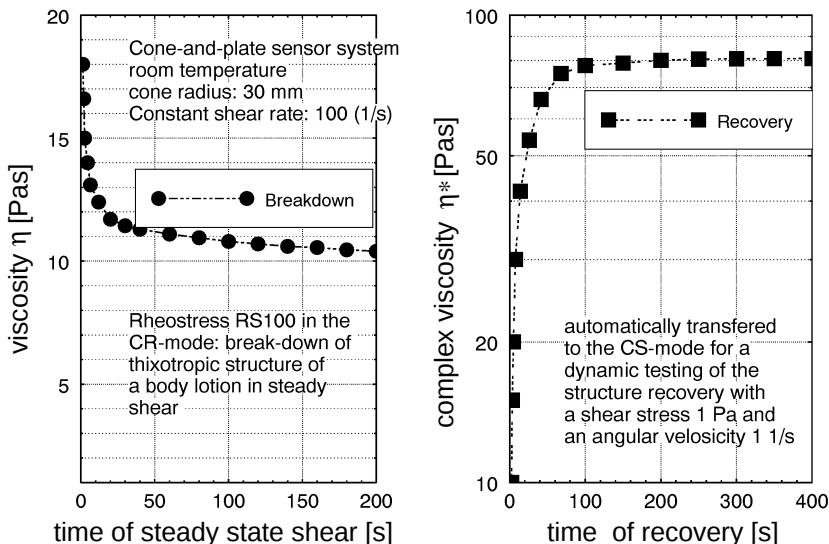


Fig. 83 Breakdown and recovery of the thixotropic structure of a body lotion

Fig.83 is a plot of the two phases of a breakdown and recovery test of a highly thixotropic body lotion. In a preliminary test one has to determine the optimum conditions of constant shear rate and of that shear time required to fully destroy the thixotropic structure, i.e. transform the gel to a sol. This breakdown of the structure can be monitored in the diagram of viscosity versus shear time. In this example the shear time and/ or the applied shear rate were not sufficient to let the viscosity reach at a constant level.

Once the suitable instrument settings have been established for the first test phase with the rheometer working in the CR-mode, the software can automatically switch the rheometer to the CS-mode and apply dynamic testing for the second recovery phase. One can plot – as in this case – the complex viscosity η^* versus time but one equally use G' or G'' . This particular body lotion regains most of its gel structure within one minute while for printing inks recovery times of several hours are not unusual.

The dynamic test is very well suited to allow the monitoring of the rebuilding of thixotropic structures, because working with very small stress amplitudes and medium frequencies the sample molecules or fillers are not hindered to freely rebond. Only CS-rheometers such as RheoStress RS100 are equipped with air bearings to provide the sensitivity to monitor the changes of moduli and the phase angle as a function of the regeneration time.

5. The Relevance of Shear Rates on Rheological Data and on the Processability of Visco-elastic Fluids

The shear rate dependency of many non-Newtonian fluids such as paints, food stuffs or polymer melts is quite astonishing: as in the case of the PMMA-melt (Fig. 15 on page 32) viscosity can drop about 3 decades as a function of 6 or more decades of shear rate. This already very wide viscosity range is still further increased in the case of samples known for their yield value which represents an infinite viscosity when subjected to below-the-yield stresses. Reporting a single viscosity value and its corresponding shear rate for any sample is of limited value to provide information about the composition of a sample and its processability unless one just uses a particular set of test conditions with an assigned shear stress or shear rate value for a quick comparison of similar samples.

If an engineer wants to use measured viscosity data to define a realistic motor rating for the drive of a mixer or extruder or if a chemist in a paint factory wants to have a closer look at processes such as painting with a brush or a paint coat that sags off vertical walls, then relevant shear rates must be established to make the measured viscosity results meaningful. In the following a number of examples are given, in which by means of simple calculations the magnitude of applicable shear rates are determined. Inasmuch as always a number of assumptions for the process parameters have to be made, the resulting calculated shear rates may easily vary from one person to the next. For this shear rate estimation one does not need to differentiate between $\dot{\gamma} = 1260$ and 1280 1/s. In most cases it will be sufficient to know that the shear rate of paint brushing is in the vicinity of $\dot{\gamma} = 5000$ 1/s and not 50 or even 0.5.

When establishing relevant shear rates for technical processes or for typical application it is important to note that in almost all cases highly different shear rates apply to different phases of a particular production or a sample's usage. Three examples are given:

5.1 Shear rates in polymer processing

For decades books on polymer engineering list as relevant shear rates in processing:

compression moulding	→ up to 100 1/s
pipe extrusion – at the die	→ up to 1000 1/s
injection moulding at the nozzle	→ up to 10000 1/s

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This seems to be a very simplified view of the reality. Shear rates do not only appear at the extruder dies but also in all other segments of the whole processing flow within an extruder or injection moulding machine. As an example of such a segment may be mentioned the flow of melt along the screw channel, the mixing flow perpendicular to the flight channel and the leakage flow from any screw flight to the trailing flight. Volume elements of the molten polymer at any point of a screw are simultaneously subjected to different types of flow which open up a range of shear rates of approx. $\dot{\gamma} = 0.01$ 1/s to well above $\dot{\gamma} = 1000$ 1/s. Under these conditions it is difficult to define any really relevant value of viscosity for such a volume element in a 3 dimensional stress situation and foresee whether good or bad processing conditions in the metering section of an extruder screw – perhaps the level of the melt homogeneity – are related to the low or upper end of the given shear rate range.

In a process such as mould filling in injection moulding machines it can also be shown that not a single shear rate but a shear rate range often covering more than 4 decades prevails: injection through a capillary-type nozzle at up to $\dot{\gamma} = 10000$ 1/s, flow while filling a mould at some $\dot{\gamma} = 100$ to 1000 1/s and flow in the after-pressure phase to keep the mould fully filled against the temperature related shrinkage of the hot melt in a cold mould at an approximated shear rate of perhaps less than $\dot{\gamma} = 1$ 1/s.

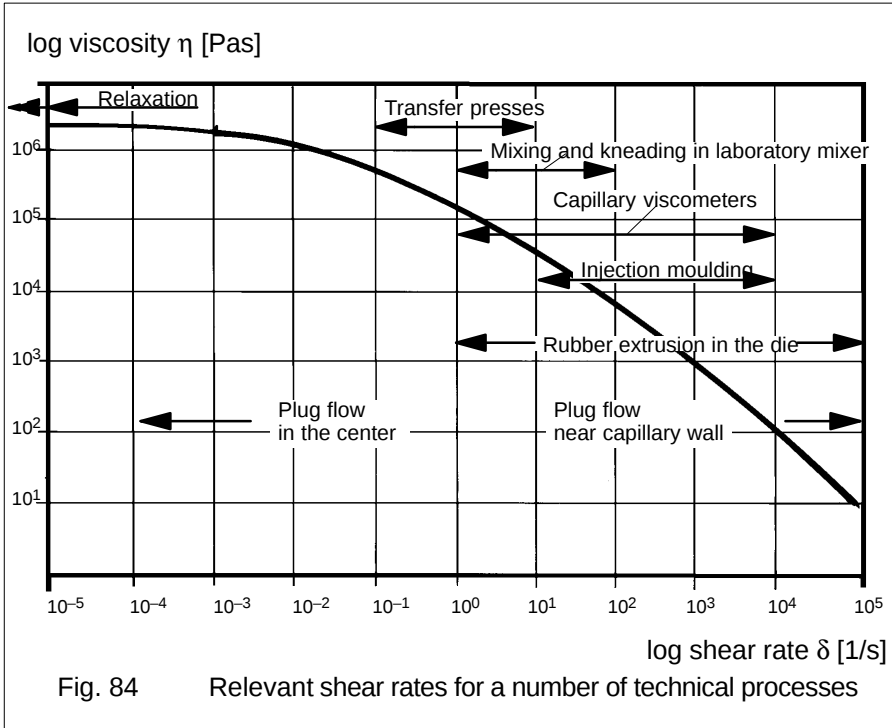
Polymer melts are not only viscous but they are also to quite an extent elastic. Elastic deformations of molecules and/or volume elements will relax with time. Most relaxation will take place once the polymer has come to a standstill at the end of extrusion or when the molded part has been removed from the mould. In sheeted or extruded polymers of high molecular-weight having cooled to room temperature, the elastic deformations – the extended spring-type elements – are “frozen-in” in the solidified polymer. They may be freed even at room temperature by what is known as “microflow” on the molecular level in hours, days or perhaps weeks and result in i.e. warping or long-term crazing in transparent parts. The release of spring-element tensions is opposed and retarded by the more viscous components in the polymer compound which will have reached their very high viscosity of almost “zero shear rate” when the extrudate has come to a standstill. Even in polyethylenes at a melt temperature of about 205°C this “zero shear viscosity” is of the order of $\eta_0 = 1000000$ Pas and at lower temperatures it is still much higher. An estimation of the relevant shear rate of relaxation will be close to $\dot{\gamma} = 10^{-5}$ 1/s – this equals a relaxation period of some 28 hours. Under these conditions the decay of the elastic stresses in thermoplastic polymers or in rubber compounds is indeed a long term-process.

Considering both the production processes and the release of frozen-in stresses as explained for polymers, then the relevant shear rates may cover a range of almost 10 decades – Fig 84. This is a range that no single rheometer

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can hope to cover, apart from the fact that measuring a viscosity curve for this shear rate range requires very long testing times.



If research problems or specifications of quality control require viscosity data of such a wide shear rate range, it has the consequence that the use of several different types of rheometers – rotational and capillary – must be considered. Each of those covers a shear rate range of 3 decades at the most. They are designed to cover different parts of the whole shear rate range so that their combination comes close to the required total range – Fig. 85.

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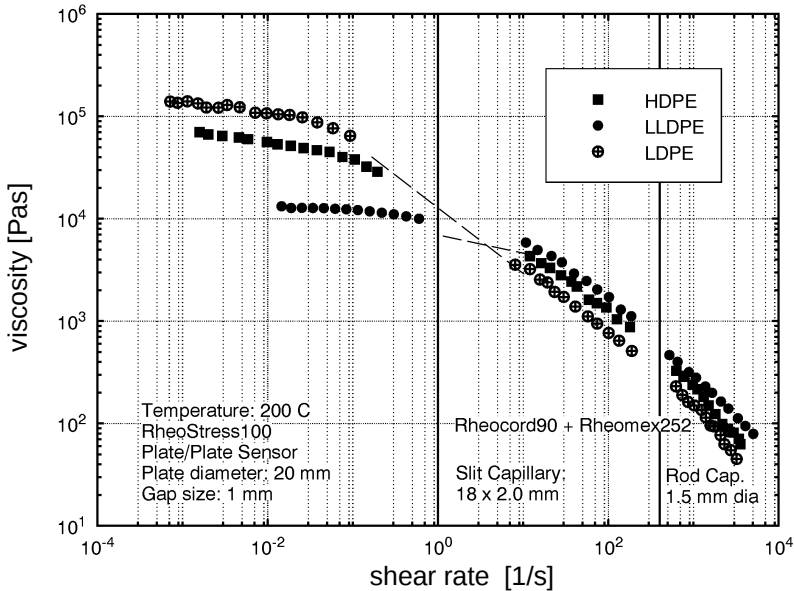


Fig. 85 RheoStress + Rheocord90: Viscosity curves of 3 PE-polymers

Deviations from a standard viscosity curve at the low or the high end of the shear rate range must be checked and graded as to their technical importance for example with respect to melt homogeneity, die swell of the extrudate and long-term dimensional stability of extruded profiles or molded parts.

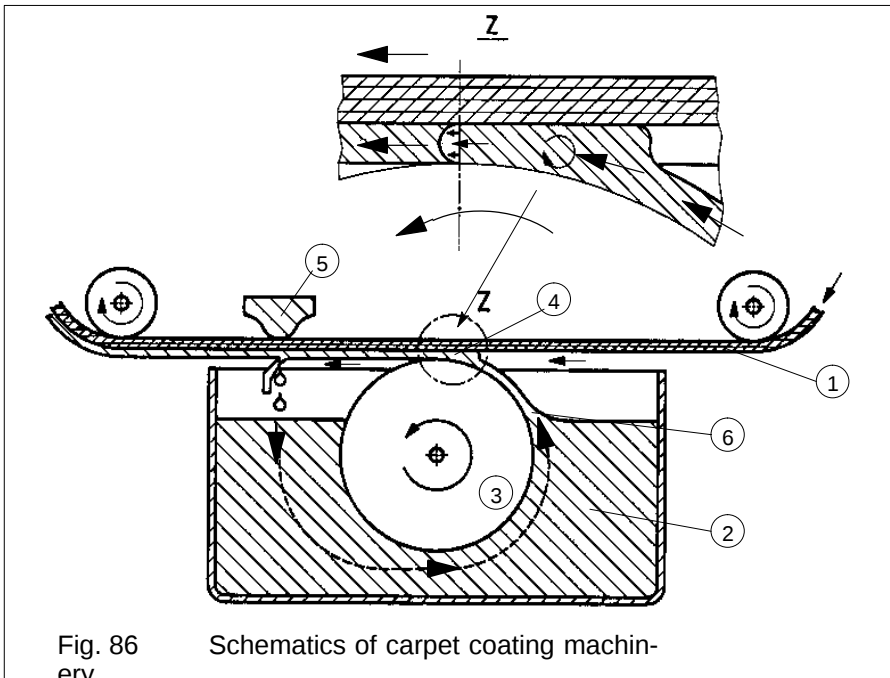
The question as to what is a relevant shear rate in polymer processing cannot be answered in general terms. One must look at the different aspects or phases of production processes.

Please note: The requirement for a very wide shear rate range to describe well conditions in steady state flow for non-Newtonian fluids finds its complement in a wide range of frequency applicable for the proper evaluation of visco-elastic substances by means of dynamic testing. Since molecular structures are best indicated at very low values of ω and elasticity dominates viscosity only at high frequencies the relevant frequency range often exceeds 6 decades. The actually available frequency range may further be expanded making use of the time-temperature WLF-superposition – as explained in chapter 9.6 in order to cover up to a 10 decade frequency range while keeping the total test time within reasonable limits.

5.2 Applying a latex layer to a carpet in a continuous process

Wall-to-wall industrial carpets are often upgraded by a foamed latex layer to provide a soft feeling when walking over it. In this context the process of applying such a latex from underneath onto the carpet continuously is discussed with respect to the various shear rates:

The machinery used has the following elements – Fig.86:



The carpet (1) is rolled off a drum and is passed over a large tank (2) filled with the latex. A rotating cylinder (3) partly submerged into the latex drags up a film of it and applies it onto the bottom side of the carpet at point (4). The sandwich of carpet and latex layer is passed through a doctor blade set-up (5) with a preset gap width to insure a uniform latex thickness. All excess latex not allowed to pass under the doctor blade is forced to drip back into the latex tank to flow slowly back to that region (6) where the cylinder (3) takes it up again for a new run.

Assuming a travel speed of the carpet of 60 m/min and a doctor blade gauge of 0.5 mm for the latex layer the shear rate at (5) is close to $\dot{\gamma} = 660$ (1/s). The latex having dripped back into the tank (2) flows back to (6) as the result of gravity

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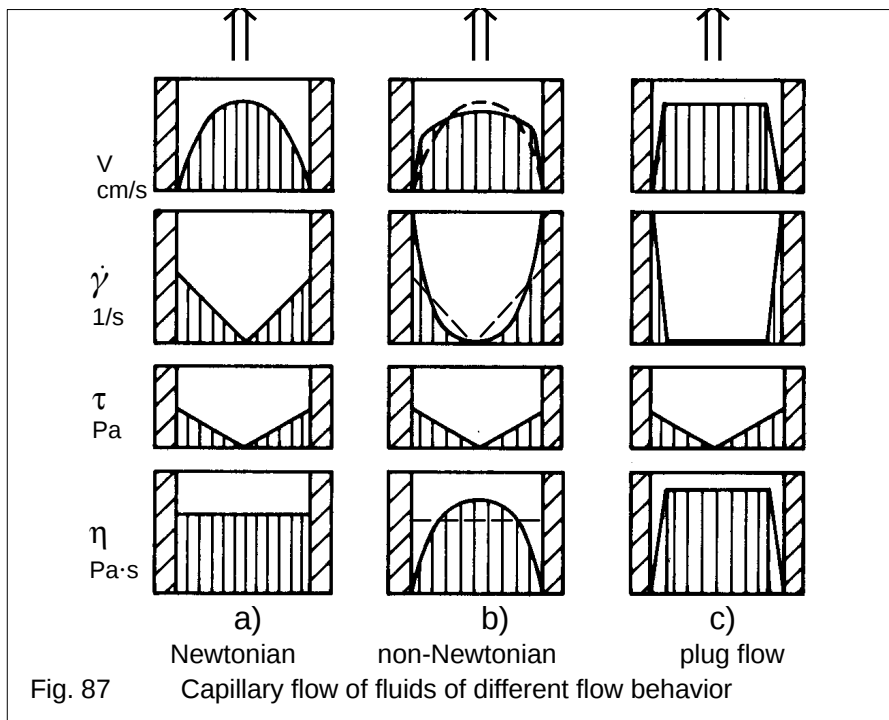
Rheology

and the shear rate that corresponds to this flow is probably not higher than $\dot{\gamma} = 1/100$ 1/s. The shear rate at (4) cannot simply be determined by dividing the carpet travel speed by the thickness of the latex layer, since one may assume that both carpet speed and the circumferential speed of the cylinder (3) are equal. Only a speed differential would contribute some shear rate on the latex. But the carpet and the surface of the cylinder form a wedge into which the latex is drawn creating a latex pressure at (4). It is this pressure which will provide a more or less parabolic flow pattern of the latex in the gap between the equally moving surfaces of the bottom side of the carpet and the cylinder. This velocity profile as it is known similarly in capillary rheometry is linked to a representative shear rate, which in this case may be estimated as $\dot{\gamma} = 1$ to 10 1/s.

Reporting this case of carpet coating should draw the attention of the reader to the fact, that very many processes we encounter in industry are not subjected to one single shear rate but to a shear rate range that in very many cases covers 3 to 4 decades. If the viscosity at (5) is high at the given shear rate a high – perhaps too high – tensile stress acts on the carpet being pulled through the doctor blade gap. If the viscosity is highly shear-thinning, too much of the latex drips off at this point. If the latex, that was forced back into the tank, rethickens at almost zero shear rate too much then the latex cannot flow back to (6) fast enough with the result that the cylinder almost runs dry and thus cannot pick-up sufficient latex.

A process as the one described may fail because the viscosity is not right at the high shear rate level but equally because the viscosity is too high at low shear rate. Considering the different phases of a production process will lead to the right evaluation of the relevant shear rate in each phase.

5.3 The problem of plug flow



Daily experience shows that squeezing toothpaste out of its tube provides a cylindrical plug which being a semi-solid just sits on the bristles of the tooth brush. Toothpastes but also very many other fluids such as highly filled polymer melts or rubber compounds containing some 30% or more of carbon black are characterized by their distinct yield values. Extruding them through capillaries often leads to a flow pattern across the diameter that differs greatly from the parabolic flow speed of Newtonian liquids. If the stress decreasing from the capillary diameter inwards drops below the value of the yield value of e.g. the toothpaste, the center of the extruded mass moves forward as a solid plug. There is no shear exerted on the mass inside of the plug and its viscosity is infinite in the plug region. Actual shear is concentrated in the ring-type layer of the mass located between the inner plug and the capillary wall – sometimes a fraction of a millimeter thick – and as a result of it the mass is highly shear-thinned. Often this ring-type layer acts as some kind of low viscous “lubricant” for the extrusion of the inner plug. High shear may additionally lead to a phase

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separation in a watery compound squeezing out a thin water layer which additionally provides lubrication for the inner plug.

Using the equations developed by Hagen-Poiseuille for the flow of Newtonian liquids leads to totally erroneous results for the shear rate and the viscosity of materials that exhibit plug flow. Calculation of any “mean” shear rate across the capillary radius does not make sense in such a case.

One has to determine the magnitude of the yield value at zero shear and look at high shear properties of the mass in narrow gap sensors of rotational rheometers. Relevant shear rates for fluids with the tendency of developing plug flow are therefore not some $\dot{\gamma} = 500$ or 1000 $1/s$ but “zero” in the center of the plug and perhaps $\dot{\gamma} = 10^4$ or even 10^5 $1/s$ in the ring-layer close to capillary wall.

5.4 Examples for an estimation of a relevant shear rates related to some typical processes.

This must be an estimation of the magnitude of shear rates within limits of a factor of ten. This estimation may use the simple equation:

$$\text{shear rate} = \frac{\text{maximum speed}}{\text{gap size}} = \frac{v}{y}$$

5.4.1 Paint industry

Paint, when applied, is subjected to both very high and very low shear rates.

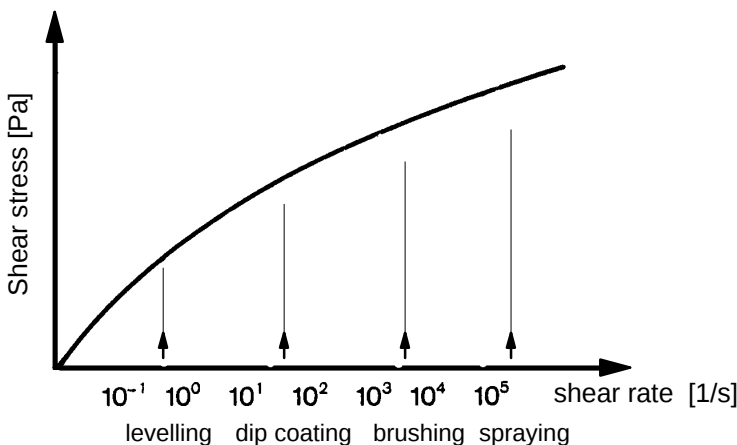


Fig. 88 Typical shear rates encountered in processing paints.

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In normal processing, paints encounter a wide shear rate range.

When paint is scooped out of a can, the shear rate can be estimated as $\dot{\gamma} = 10 \text{ (s}^{-1}\text{)}$.

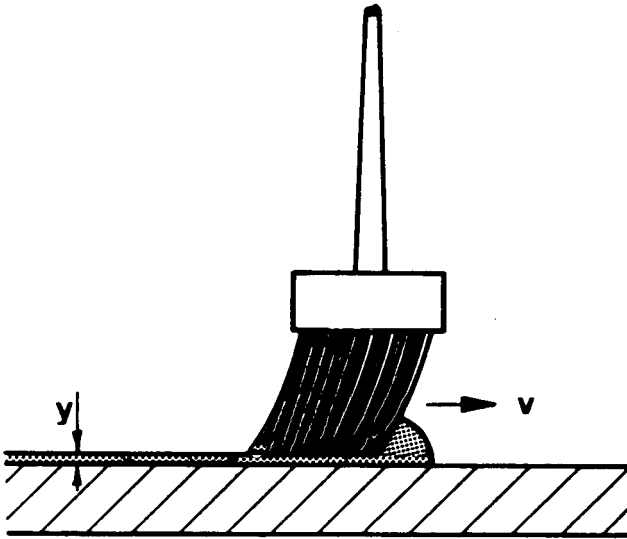


Fig. 89 Brushing paint onto a flat surface

Estimation of the shear rate of brushing:

During application, the brush can be drawn across a board at a speed of $v = 1\text{m/sec} = 1000 \text{ mm/sec}$

The thickness of the paint layer is estimated as

$$y = 0.2 \text{ mm}$$

then the shear rate of brushing is approximately:

$$\dot{\gamma} = \frac{1000}{0.2} = 5.000 \text{ s}^{-1}$$

Paint sprayed out of the nozzle of an air gun is subjected to shear rates exceeding $\dot{\gamma} = 50.000 \text{ s}^{-1}$.

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A coat of paint brushed onto a vertical wall tends to sag off under the influence of gravity.

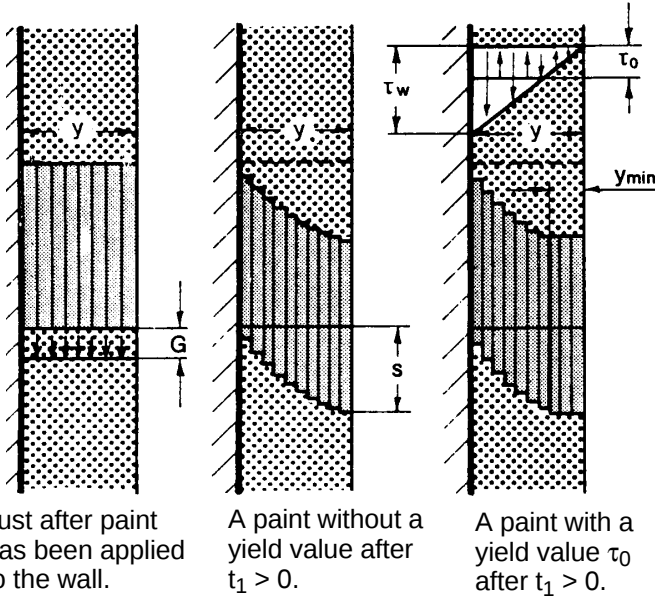


Fig. 90 Paint sagging off a vertical wall

The shear stress at the wall τ_w which exists at the boundary A between the layer of paint and the wall, is

$$\tau_w = \frac{G}{A} = \frac{A \cdot (h - y) \cdot \rho \cdot g}{A} = (h - y) \cdot \rho \cdot g \quad [66]$$

τ_w = shear stress at the wall [Pa]

τ_0 = yield value [Pa]

G = weight of the paint layer acting on A [N]

A = surface area on the wall [m²]

h = thickness of the paint layer [m]

y = variable in the horizontal (h)-direction [m]

ρ = density of the paint layer [kg/cm³]

g = acceleration of gravity [m/s²]

v = sagging speed in the vertical direction [m/s]

s = distance the paint sags within a period t [m]

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Shear rate is: $\dot{\gamma}_w = \frac{\tau_w}{\eta} = \frac{(h - y) \cdot \rho \cdot g}{\eta} \quad [1/s]$

Integration of $dv = \dot{\gamma} = \frac{dv}{dy}$ results in a rate of sagging v :

$$v = \rho \cdot y \cdot h \cdot g / \eta - \rho \cdot y^2 \cdot g / 2 \cdot \eta \quad [m/s]$$

for a Newtonian liquid: $V_{\max} = \rho \cdot g \cdot h^2 / 2 \cdot \eta = \dot{\gamma}_w \cdot y / 2$

In case of non-Newtonian fluid such as a Bingham fluid the shear stress is:

$$\tau = \tau_0 + \eta_B \cdot \dot{\gamma}$$

for $\tau_0 \geq \tau \rightarrow \dot{\gamma} = 0$ i.e. the paint layer does not flow.

for $\tau \geq \tau_0 \rightarrow$ a layer $y_{\min}$ will sink down as a solid slab on a layer $(h - y_{\min})$ flowing at a speed v , which is related to the shear dependency of the paint.

Example for a paint not showing a yield value:

$$y = 0.1 \text{ mm} = 0.0001 \text{ m}$$

$$\rho = 1.1 \text{ g/cm}^3 = 1100 \text{ g/m}^3$$

$$g = 9.81 \text{ m/s}^2$$

$$\eta = 2.0 \text{ Pa} \cdot \text{s} \quad \text{at } \dot{\gamma} \approx 1 \text{ s}^{-1}$$

$$\tau_w = 0.0001 \cdot 1100 \cdot 9.81 = 1.08 \frac{\text{N}}{\text{m}^2} = \text{Pa}$$

$$\dot{\gamma}_w = \frac{\tau_w}{\eta} = \frac{1.08}{2} \approx 0.5 \frac{\text{Pa}}{\text{Pa} \cdot \text{s}} = \frac{1}{\text{s}} = \text{s}^{-1}$$

$$v = \frac{0.5 \cdot 0.1}{2} = 0.025 \text{ mm/s} = 1.5 \text{ mm/min}$$

Under the condition that the paint does not exhibit a yield value and there is no viscosity increase in the paint layer due to solvent evaporation or due to solvents adsorbed into a porous wall, the length s of the downward sagging of the paint layer within a period of $t = 60 \text{ s}$:

$$s = v \cdot t = 0.025 \cdot 60 = 1.5 \text{ mm}$$

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A paint will only flow off a vertical wall when the shear stress at the boundary is higher than the shear stress τ_0 .

$$\tau_w = \gamma \cdot \rho \cdot g \geq \tau_0$$

This means that sagging will only occur when the thickness of the paint layer $y_{\min}$ is bigger than:

$$y_{\min} \geq \frac{\tau_0}{\rho \cdot g}$$

Paints are complex dispersions of liquids, fillers, pigments and processing aids etc. They belong always to the group of non-Newtonian fluids. Their viscous and elastic properties defining their processibility are highly dependent on the the shear rate relevant to the different phases of production or application. There is no single "correct" shear rate, but a relevant shear rate range often covering several decades. The specialist in a paint factory may vary the rheological behavior of his paints by altering the paint components their percentage in a paint formulation and/or the intensity of the mixing process. In doing so he may look for an acceptable compromise so that fillers will not sediment and form a "cake" on the bottom of tins ($\dot{\gamma} \approx 0$ 1/s). He may want to prohibit, that his paints sag off vertical walls even with thicker coatings (small values of $\dot{\gamma}$), or he may look for an easy brushing ($\dot{\gamma} \approx 5\,000$ 1/s) or spraying ($\dot{\gamma} \approx 50\,000$ 1/s).

Practical experience has shown that differences in processibility of paint batches – good or bad – are more often related to their flow behavior at very low than at very high shear rates. This is contrary to the opinion that applying paints is a coating process mainly controlled by high shear rates.

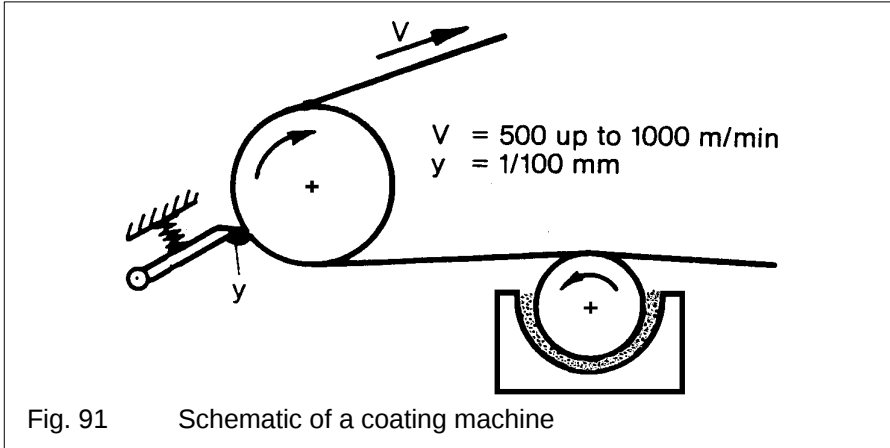
These considerations have not yet included the elastic properties of paints, which also influence the processibility of paints.

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5.4.2 Paper coating

Quality papers are coated to get a smooth and often glossy surface.



Typical production conditions in a continuous coating process are:

Paper speed $v = 500 \text{ m/min}$ (up to 1000 m/min)

$$v = 50000 \text{ cm/min}$$

$$v = \frac{50000}{60} \text{ cm/s}$$

Gap size y = distance between the nip of the scraper blade and the roll surface

$$y = \frac{1}{100} \text{ mm} = \frac{1}{1000} \text{ cm} = 10^{-3} \text{ cm}$$

$$\text{Shear rate } \dot{\gamma} = \frac{50000}{60} \cdot 10^3 = 8.3 \cdot 10^5 \text{ s}^{-1}$$

Maximum shear rates in paper coating can exceed values of 10^6 s^{-1} .

5.4.3 Engine oil performance

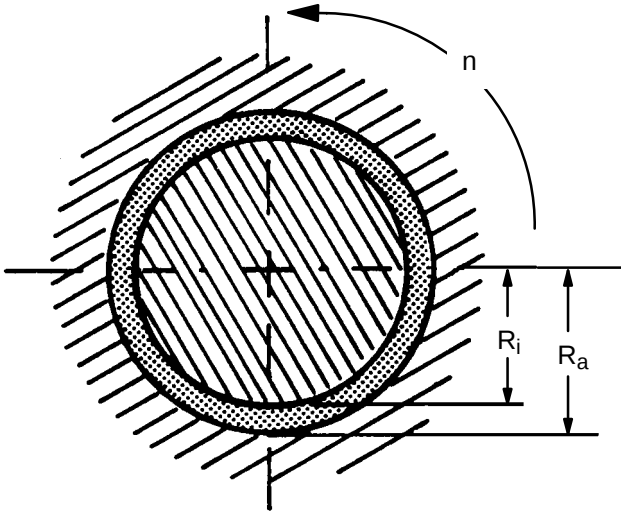


Fig. 92 Cross section of a crankshaft sleeve bearing showing annular gap for the lubricant.

Typical dimensions are:

- R_i = Radius of the shaft = 27.53 mm
- R_a = Radius of the sleeve = 27.50 mm
- y = Oil film thickness = 0.03 mm
- n = Rotational speed of crank shaft = 4000 min⁻¹

$$\delta = \frac{R_a}{R_i} = 1.00109$$

$$\delta^2 = 1.00218$$

$$\dot{\gamma} = \frac{\pi}{15} \cdot \frac{\delta^2}{\delta^2 - 1} \cdot n$$

This will lead to $\dot{\gamma} \approx 4 \cdot 10^5 \text{ s}^{-1}$

The shear rates indicated in literature for this problem vary from $\dot{\gamma} = 10^4 \text{ 1/s}$ for conditions when starting an engine to $\dot{\gamma} = 10^6 \text{ 1/s}$ encountered in sport cars at full speed.

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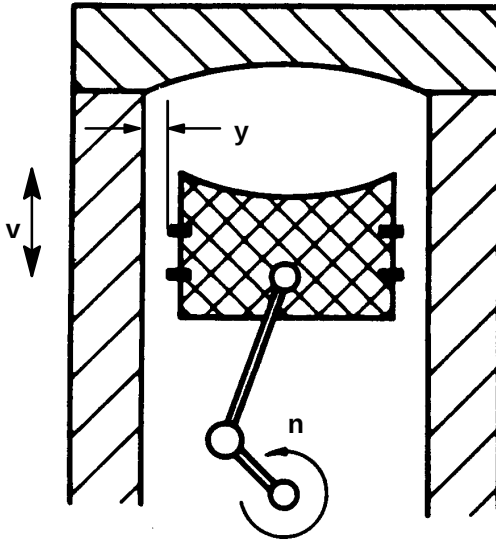


Fig. 93 Cross section of an engine cylinder and its piston to define the parameters.

Typical dimensions are:

y	=	Gap size = 0.03 mm
n	=	Rotational speed of the crankshaft = 4000 min ⁻¹
$v_{\max}$	=	Maximum speed of the piston = 20 m/s
v_{mean}	=	Mean speed of the piston = 14 m/s

This leads to:

$$\dot{\gamma}_{\max} = \frac{v_{\max}}{y} = \frac{20.000 \text{ mm/s}}{0.03 \text{ mm}} \approx 6.7 \cdot 10^5 \text{ s}^{-1}$$

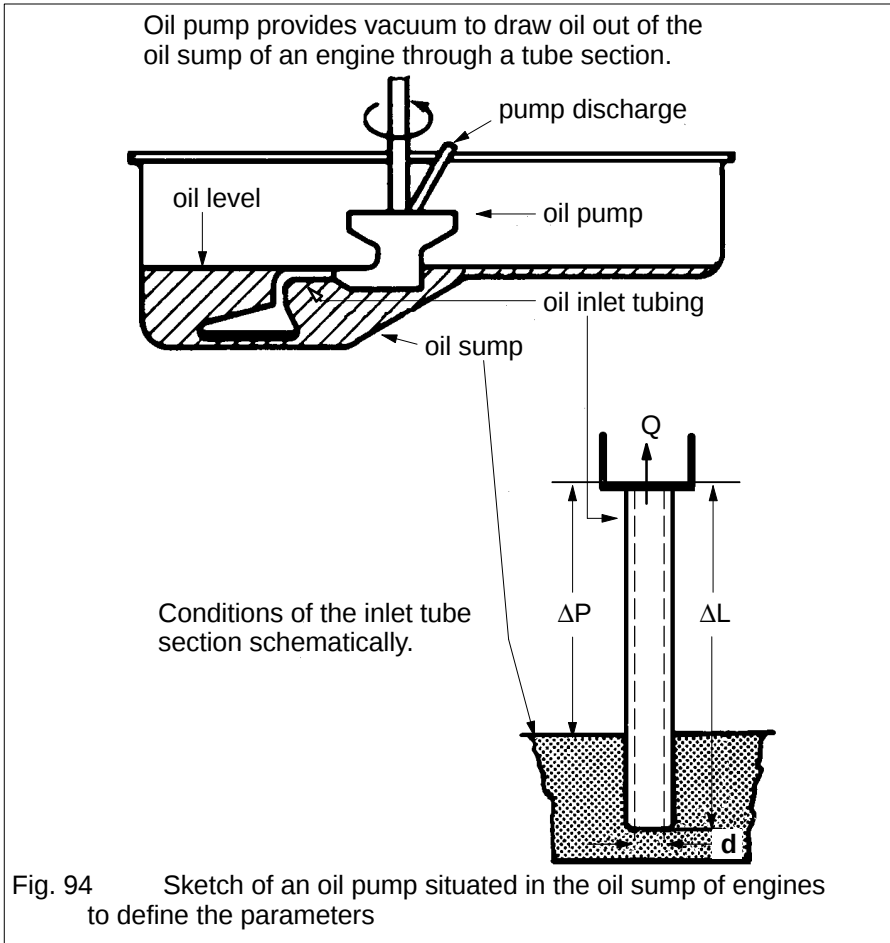
$$\text{or } \dot{\gamma}_{\text{mean}} \approx 4.7 \cdot 10^5 \text{ s}^{-1}$$

Shear rates between piston rings and the cylinder obviously reach extremely high levels.

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Sucking oil from the oil sump of an engine



Typical dimensions are:

d = Tube diameter = 0,7 cm = 7 mm

R = Tube radius = 0.35 cm = 3.5 mm

Q = Flow rate = 30 cm³/min = 500 mm³/s

$$\dot{\gamma} = \frac{4}{\pi} \cdot \frac{Q}{R^3} = \frac{4}{3.14} \cdot \frac{500}{3.5^3} \approx 15 \text{ s}^{-1}$$

Shear rates encountered by engine oils in the inlet tube section of the oil pump are very low. Shear rates are even lower in the oil sump itself.

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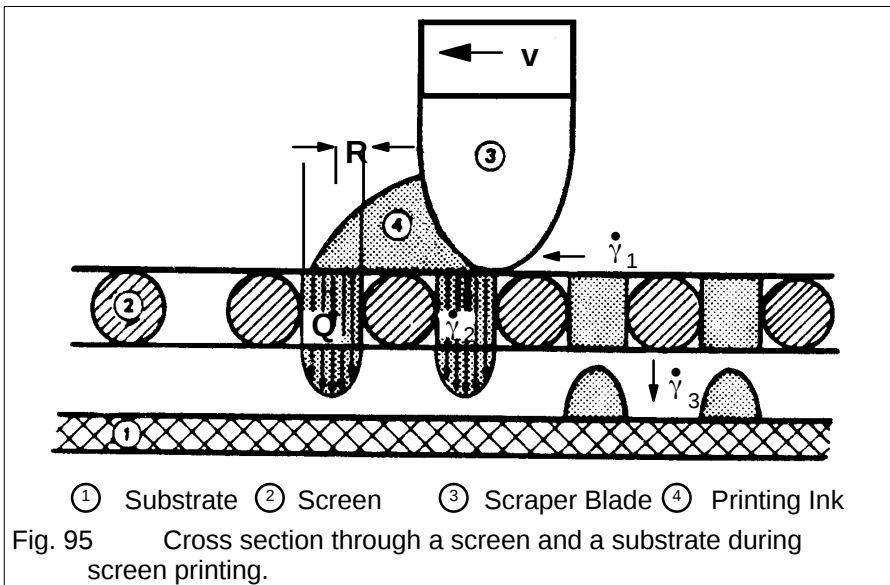
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Engine oils are not just subjected to one shear rate but rather to a very wide shear rate range. This is important to know in spite of the fact that oils are normally Newtonian. Motor oils are subjected to greatly changing loads over a wide temperature range. To maintain sufficient lubricity for this difficult application suitable ingredients are added to top-class oils, which make these oils non-Newtonian.

This should make oils sufficiently viscous at high shear to prevent metal contact between the parts to be lubricated. The oil must be low enough in viscosity at low shear rates when flowing in the oil sump under gravity towards the inlet tube of the oil pump and then upwards through that inlet tube being sucked by that pump. If the oil is too thick the pump may draw partly air and then starve the oil supply to the bearings. Very important is that under extremely cold conditions the oil does not exhibit a yield value (i.e. at zero shear rate) or it will behave as a solid and not flow into the inlet at all.

5.4.4 Screen printing

The estimation of the shear rate when ink is squeezed through a screen may follow this procedure:



Determine the speed v of the scraper blade passing over one orifice: Knowing the type of mesh to the screen will give a mean orifice width and assuming the orifice being round a mean radius R . The time t for the scraper to pass over one orifice can be calculated.

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$$t = \frac{2R}{V}$$

Determine the volume V that passes through one orifice: Print on a substrate to cover a defined area. Then weigh the ink on the substrate to get the weight G . Determine the number N of orifices per square area. Knowing the density ρ of the ink will allow to calculate V :

$$V = \frac{G}{N \cdot \rho} [\text{mm}^3]$$

The flow rate Q can now be calculated:

$$Q = \frac{V}{t} [\text{mm}^3/\text{s}]$$

The orifice is considered to be a section of a capillary, therefore one can now calculate the shear rate with equation [18]:

$$\dot{\gamma} = \frac{4}{\pi} \cdot \frac{Q}{R^3} [1/\text{s}]$$

Typical values are:

$$G = 1.8 \cdot 10^{-5} \text{ g/mm}^2$$

$$N = 10 \text{ 1/mm}^2 \text{ in a 31 mesh screen}$$

$$\rho = 1.2 \cdot 10^{-3} \text{ g/mm}^3$$

$$V \approx 1.5 \cdot 10^{-3} \text{ mm}^3$$

$$v = 30 \text{ mm/s} \approx 18 \text{ m/min}$$

$$R = 45 \cdot 10^{-3} \text{ mm}$$

$$t = 3 \cdot 10^{-3} \text{ s}$$

$$Q = 0.5 \frac{\text{mm}^3}{\text{s}}$$

This leads to:

$$\dot{\gamma}_2 = 6900 \text{ s}^{-1} \text{ in a 31 mesh screen}$$

The printing ink will be subjected to a much higher shear rate between the surface of the screen and the scraper blade = $\dot{\gamma}_1$. Flowing into the substrate will mean lower shear rates = $\dot{\gamma}_3$. Yield points and a thixotropic structure will help the ink to give and maintain a crisp printing outline.

Summary: Screen printing is a multiple shear rate application. Being highly non-Newtonian, viscosity measurements must look at both the low and the high shear rates.

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5.4.5 Lipstick application

The estimation of the shear rates encountered when applying lipstick may follow this procedure:

A panel of not less than 10 women applies lipstick in a single stroke. The coating speed v during this stroke is timed. The lipsticks are weighed before and after the application to get a mean weight G of such a lipstick coat. Blotting paper pressed onto the coated lips will mark the area A which has been coated. This area will be measured by means of a planimeter.

The coat thickness is determined by

$$y = \frac{G}{A \cdot \rho}$$

ρ = Density of the lipstick

Typical values are:

$$v = 10 \text{ cm/s}$$

$$G = 0.05 \text{ g}$$

$$A = 10 \text{ cm}^2$$

$$\rho = 1 \text{ g/cm}^3$$

$$y = 0.005 \text{ cm}$$

Shear rate in lipstick application: $\dot{\gamma} \approx 2\,000 \text{ s}^{-1}$

5.4.6 Some other shear rates $\dot{\gamma} [\text{s}^{-1}]$

Applying hand lotion	10 000 to 20 000
Buttering bread	10 to 50
Blood flow (area of major interest)	0.1 to 250
Extrusion of liquid cream from plastic bottle	5 to 10
Pouring from a bottle	50 to 200
Forcing a medicine through a hypodermic syringe	1 000 to 10 000
Pumping liquid chocolate through a pipe 10 cm dia. 50 l/min	30
Hydraulic iron ore particle transport through a pipeline	~ 600
Passage through an aerosol valve	10^4

6. Optimization of Rheometer Test Results

Good test results can only be achieved by an optimum combination of a suitable rheometer with the thoughtful selection of test parameters by the users. These two essential factors are looked at separately.

6.1 How accurate are capillary and falling ball viscometers?

All capillary rheometers used for the viscosity measurement of Newtonian liquids such as Ubbelohde or Cannon-Fenske are related to the kinematic viscosity of water, which is internationally established as $\nu = 1.0035 \text{ [mm}^2/\text{s]}$ at 20°C . In capillary viscometry the measured test value is subjected to the parameters of the calibration constant c_{cap} related to the dimension of the capillary, the actual temperature T of the liquid, the density of the liquid ρ and the flow rate Q , i.e. the time for a defined volume to pass through a segment of the capillary:

$$\text{kinematic viscosity } \nu = \nu(c_{\text{cap}}, T, \rho, Q)$$

Each type of capillary used is only applicable for a limited viscosity range. Governmental authorities in most countries provide standard viscosity liquids which link in a stepped-up procedure the calibration constant of the first capillary to the water viscosity ν_1 . This first capillary is then used to measure the viscosity ν_2 of a higher viscous liquid. With this ν_2 -value a second capillary with an increased capillary diameter is calibrated. For a certified viscosity measurement (with respect to ν_1) of liquids of a high viscosity perhaps 10 capillaries with different calibration constants c_{cap} have to be used in successive tests.

The test parameter “temperature T ” can be measured and maintained by a suitable thermal liquid, constant temperature bath and circulator (for short: circulator) within limits of $1/1000^\circ\text{C}$.

The accuracy of timing the flow rate Q in these tests can be 0.01 s.
The accuracy for the given density can be better than 0.01%.

This means that the accuracy of these capillary viscosity data – their significance – can be guaranteed as $\pm 0.1\%$.

Calibration fluids can be bought either from the governmental test institutes or from companies supplying capillary- or rotational rheometers to allow the calibration of capillary viscometers of unknown specifications or for the comparison with the viscosity of unknown liquids. The reported viscosity data are then multiples of the viscosity of water. There are no rotational viscometers or rheometers which are as accurate as high-quality capillary viscometers. The great advantage in accuracy of top-class capillary viscometers is balanced by

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their disadvantage of being only applicable for “simple” Newtonian liquids. They are not suitable for the viscosity measurement of non-Newtonian fluids for which the shear rate across the capillary diameter is highly non-linear and it is therefore not well defined. Capillary viscometers, of course, cannot be used for fluids which are thixotropic and those possessing a yield value.

The same can be said also for “falling ball viscometers”, which are similarly calibrated in a stepped-up procedure using several calibration fluids based on the water viscosity. To meet the requirements of those fluids differing in viscosity, tests are run with such a viscometer using a set of balls with different diameters. With respect to the accuracy of their measurement results “falling ball viscometers” can be close to the accuracy of the capillary viscometers.

6.2 How accurate are rotational viscometers and rheometers?

Viscosity cannot be measured directly. It can be calculated from the relationship between shear stress and shear rate, which are linked directly to the basic units of physics (SI-units): force, length, and time.

The viscosity is defined as:

$$\eta = \tau / \dot{\gamma} = \text{force} \cdot \text{time} / \text{area} \quad [\text{N} \cdot \text{s}/\text{m}^2 = \text{Pa} \cdot \text{s}]$$

Rheometers/viscometers which subject liquids at a given temperature T to defined shear stresses and measure the resulting shear rate – or vice versa – are named “absolute rheometers” because they can link their viscosity data to the absolute units of physics – they do not require calibration fluids based on the water viscosity.

Parameters for the measurement of viscosity are:

$$\begin{aligned}\tau &= A \cdot M_d \quad \text{and} \\ \dot{\gamma} &= M \cdot \Omega\end{aligned}$$

Both coefficients A and M (shear stress– and shear rate factors of equations [12] and [13]) are linked to the geometry of the chosen sensor system and the particular type of the rheometer and they may be combined in a single instrument coefficient $G = A/M$.

Temperature is, of course, an additional important parameter.

In this context the other possible influencing factors on viscosity such as pressure P, the shear time t and the voltage V are neglected.

The influencing parameters on the measured viscosity and the accuracy of the test results are:

$$\eta = \eta(\tau, \Omega, G, T).$$

τ : precision of the assigned torque
 Ω : precision of the assigned rotor speed
geometry G : accuracy of the geometry dimensions
temperature T : precision of the assigned sample temperature

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6.2.1 The accuracy of the assigned shear stress in CS-rheometers and of the measured torque values in CR-rheometers

The shear stress is derived from the torque M_d produced on the rotor shaft by means of – as in the case of the HAAKE RheoStress RS100 – a special three phase, drag-cup motor. An assigned motor current “I” produces a resulting torque M_d according to this equation:

$$M_d = k \cdot I^2 \quad [67]$$

k = correlation coefficient

Typical torque ranges for a CS-rheometer are given;

minimum torque $\tau = 1 \cdot 10^{-6} \text{ Nm} = 1 \text{ } \mu\text{Nm}$

maximum torque $\tau = 5 \cdot 10^{-2} \text{ Nm} = 50\,000 \text{ } \mu\text{Nm}$

torque accuracy: $= \pm 1 \text{ } \mu\text{Nm}$ – see additional remarks below.

CS-rheometer must be calibrated to secure that the above specifications are indeed met. Calibration of a CS-rheometer means to determine the dependence of the assigned current to the resulting torque which is then applied for the sample to be viscosity tested. This dependence will be subject to small errors connected to an exponent deviating slightly from the exponent “2” in the above equation. Deviations are related to e.g. the torque dependence on the motor coil temperature and to the small, but not negligible rotor speed related friction within the air bearing.

A calibration by using calibration fluids is not the method of good choice inasmuch as it additionally introduces instrumental effects such as eccentricity, end effects and shear heating.

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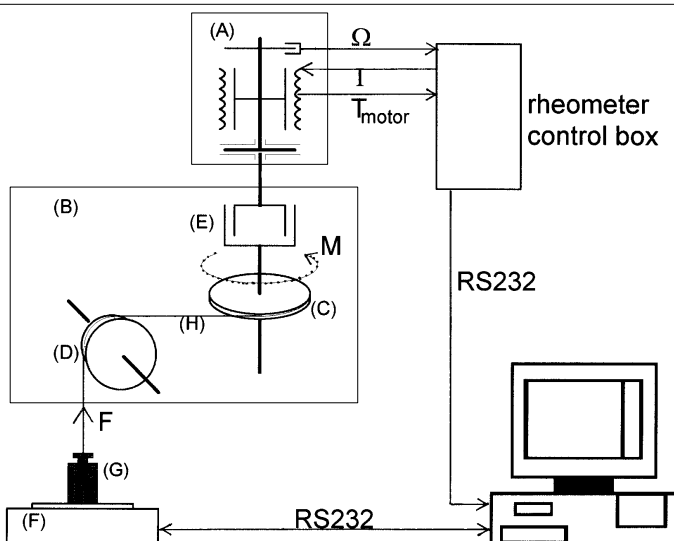


Fig. 96 a Calibration set-up for a CS-rheometer

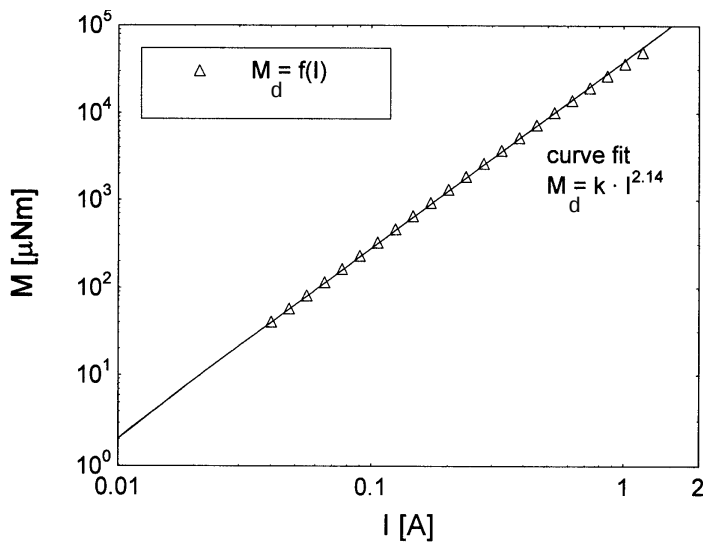


Fig. 96 b Calibration report: Input of current I versus resulting torque M_d

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Instead it is preferable – Fig. 96 a – to measure the resulting torque M_d on the rotor shaft by simply determining the force that pulls on a radius R of a pulley (C) screwed onto the rotor shaft. To turn the horizontally acting force on (C) into the vertical a second pulley (D) is used. The force is lead to a weight block G by means of a thin thread (H) passing over both pulleys. The weight block G sits on an analytical, i.e. highly accurate balance (F). For the motor current $I = 0$ the balance will indicate the calibrated weight value of G . With increasing values of the current torque values result, which tend to pull the weight block G upwards and in effect reduce the actual weight signal on the display of the balance. To minimize the friction on the pulley shafts they are supported just as the motor shaft by air-bearings.

Fig. 96 b shows a typical diagram of a computerized calibration of the assigned current I [A] versus the resulting torque M_d (μNm). A regression calculation on the data points provides in this particular case of a rheometer calibration the following equation:

$$M_d = k \cdot I^{2.14}$$

k = correlation factor

This calibration method providing the true values of k and the exponent reduces the torque measurement to a weight measurement which allows to trace the torque determination to the basic standards of mass and length – pulley radius. The used balance can be certified by their manufacturers with a tolerance range of ± 0.2 mg. This calibration setup allows to calibrate the torque of a CS-rheometer under static ($\Omega = 0$) and under dynamic ($\Omega > 0$) conditions. The reproducibility of these torque measurements is $\pm 1 \mu\text{Nm}$.

The actual applied torque will additionally depend on the angular velocity of the rotor, on the friction in the air-bearing within the extremely narrow gaps of these bearings and on the change of the motor rating as the result of increased temperature in the motor coil at higher torque values. All of these errors effects on the current/torque dependence are actually determined by this calibration which assigns defined current values and provides corrected controlled stress values within a torque range covering more than 4 decades. The calibration data and curve-fitting procedures are used to allow a suitable software correction of the instrument coefficients.

It remains a tolerance limit for the assigned torque of $\pm 1 \mu\text{Nm}$ for torques below $100 \mu\text{Nm}$ which is mainly provided by the friction within the air-bearing and which cannot be completely compensated. For this torque range the percentage of the above tolerance becomes increasingly less significant as much as $100 \mu\text{Nm}$ are approached. For higher values of torque the accuracy of these CS-torque data stays within the stated tolerance range.

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As the result of the air-bearings which are a special feature of the CS-rheometers they can measure torque values which are about a factor of 100 below the minimum torques that are usual for good CR-rheometers with roller bearings. This is an important feature when the rheological behavior of semi-solids and fluids are to be determined at very low shear rates, i.e. below or just above their yield values.

In CR-rheometers/viscometers with spring-type torque sensors the accuracy of the measured torque is mainly dependent on the linearity of the spring-coefficient. The accuracy of the shear stress measurement of these rheometers within their limited shear stress range is rated as 0.5% of their maximum torque. Calibration of CR rheometers with respect to their torque sensors makes also use of the mechanical method of applying defined torques – a weight acting on a defined radius – and plotting the resulting torque signals versus the applied torques. Such a calibration which operators may want to perform on their instruments in regular intervals of weeks or months may only take minutes and it is much less troublesome and time-consuming than the calibration with calibration fluids.

6.2.2 The significance of the rotor speed (strain and angular velocity)

In conventional CR-viscometers the rotor speed is controlled by means of a tachometer generator attached to the drive motor, which permanently checks the deviation between the assigned rotor speed and the actual rotor speed as determined by the tachometer generator. While this setup of a speed sensor is quite acceptable at high rotor speeds the significance of low speed signals as the result of small tachometer-generator currents leaves much to be desired.

Modern CS-rheometers use incremental angular displacement sensors which define a full revolution in 1 000 000 angular increments ± 1 . Very low values of shear rate are determined by plotting the rate of deformation versus time and then by using a curve fit on this plot towards the zero shear rate. Above 10 rpm the rotor speed is directly measured with a tolerance of 0.1 %. CS-rheometers with this technique are much more accurate in their deformation/strain- and shear rate measurements than conventional CR-rheometers at both very low and high shear rates.

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6.2.3 The significance of the geometry factors which define the influence of the given geometry of sensor systems

$$\eta = A/M \cdot M_d/\Omega = G \cdot M_d/\Omega$$

For a coaxial cylinder sensor system the constant G_{cyl} is:

$$G_{cyl} = 1/4 \pi L (Ra^2 - Ri^2) \cdot 1/(Ri \cdot Ra)^2$$

Ra = Cup radius

Ri = Rotor radius

L = Rotor length

The parameter G_{cyl} dependent on the squared radii is thus influenced more by the radii than by the length of the rotor. Standard tolerance levels for the machined dimensions of the rotors can be maintained at some 0.5%.

For a cone-and-plate sensor system the constant G_{cone} is:

$$G_{cone} = 3 \cdot \alpha / 2 \cdot \pi \cdot R^3$$

The cone radius R being cubed is the most important geometry dimension.

Please note: The stated cone- or plate radius of such a sensor system is only relevant for the measured data if the sample is correctly filling the shearing gap – overfilling or under-filling extends or reduces the actual sample diameter. The significance of the geometry factor G_{cone} is only under those ideal conditions about 0.5%. It is more realistic to work with a G_{cone} -significance of 1% or even higher.

6.2.4 The significance of the assigned temperature

With good temperature control, the significance of the assigned temperature may be kept within 0.5%.

6.2.5 The tolerance level in rotational rheometry is defined by the combination of the significance levels of the mentioned parameters

$$\Delta \eta_{abs} = |d \eta / d \tau| \cdot \Delta \tau + |d \eta / d \dot{\gamma}| \cdot \Delta \dot{\gamma} + |d \eta / d G| \cdot \Delta G + |d \eta / d T| \cdot \Delta T$$

with $d \eta / d \dot{\gamma} = -\tau / \dot{\gamma}^2$ and $d \eta / d \tau = 1 / \dot{\gamma}$ the above equation can be rewritten:

$$\Delta \eta_{abs} = |1 / \dot{\gamma}| \cdot \Delta \tau + |\tau / \dot{\gamma}^2| \cdot \Delta \dot{\gamma} + |d \eta / d G| \cdot \Delta G + |d \eta / d T| \cdot \Delta T \quad [68]$$

This equation above indicates that the accuracy of the viscosity data is subjected to several, often small-size factors. The dominant one is the influence of the squared inverse shear rate: small shear rates have an enormous effect on the accuracy. Keeping this in mind modern CS-rheometers make use of very sensitive sensors for the strain- or shear rate measurement. On most CR-viscometers a less sophisticated speed control is installed.

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				Viscosity of an ideal liquid in [mPas]					
VT500	%	Val	n[rpm]	1.0	10.0	100.0	6900	10000	100000
Tau error	0.5	FS	2.0				3.4%	2.4%	
D error	0.5	AB	5.0				1.4%	1.0%	
Geo error	0.5	AB	8.3				0.8%	0.8%	
Sensor	MVDIN		10.0				0.7%		
A factor	614.0		13.9						
M factor	1290.0		20.0						
			23.2						
<Alt> G = plot graph			45.3						
<Alt> P = print table			50.0			9.5%			
			64.5			7.4%			
Note:			100.0			4.8%			
" " out of range:			107.8			4.4%			
5%..100% Range			179.6			2.7%			
			200.0			2.4%			
FS = full scale defl.			295.7			1.6%			
AB = absolute value			500.0		9.5%	1.0%			
			600.0		7.9%	0.8%			

				Viscosity of an ideal liquid in [mPas]					
VT500	%	Val	n[rpm]	1.0	10.0	100.0	6900	10000	100000
Tau error	0.5	FS	2.0						1.4%
D error	0.5	AB	5.0				8.3%	5.7%	0.6%
Geo error	0.5	AB	8.3				5.0%	3.5%	
Sensor	SVDIN		10.0				4.2%	2.9%	
A factor	3694.0		13.9				3.0%	2.1%	
M factor	1290.0		20.0				2.1%	1.4%	
			23.2				1.8%	1.2%	
<Alt> G = plot graph			45.3				0.9%	0.8%	
<Alt> P = print table			50.0				0.8%	0.6%	
			64.5				0.6%		
Note:			100.0						
" " out of range:			107.8						
5%..100% Range			179.6						
			200.0						
FS = full scale defl.			295.7			9.7%			
AB = absolute value			500.0			5.7%			
			600.0			4.8%			

markings | too low: below 5% of full scale
 in the table: || too high: above 100% of full scale

Fig. 97 Accuracy of viscosity tests related to the sensor systems MVDIN and SVDIN – sizes as sketched in Fig. 98 – used.

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To allow users of these rheological instruments to assess the accuracy that may be guaranteed for a particular package of such an instrument and its chosen sensor system, a software package has been designed which calculates the combined influences of the above listed tolerance factors. Typical tables indicating “safe” or “suitable” test conditions for two types of sensor systems are shown in Fig. 97. In this example a viscometer – HAAKE Viscotester VT550 – which allows one to choose up to 20 fixed rotor speeds within the range of 2 to 800 1/min was combined with 2 coaxial cylinder sensor systems MVDIN and SVDIN of ISO/DIN-design, which are of similar shape but differ in their surface area – defining their shear stress range – while providing identical shear rates for given speed values. The Viscotester VT500 is designed for a maximum torque of 2 Ncm and with the relevant shear stress factors A of the sensors system provides these maximum shear stresses:

$$\text{MVDIN: } \tau_{\max} = 123 \text{ Pa} \quad \text{and} \quad \text{SVDIN: } \tau_{\max} = 750 \text{ Pa}$$

The tables given by the computer– Fig. 97 – given for several Newtonian liquids and the rotor speeds provided for this viscometer lists accuracy data for those test conditions which are above 5% and below 100% of the full scale torque range: Below 5% the torque signals are considered too insignificant and above 100% of the torque range the rotor speed is too high for a given viscosity.

MVDIN: For a liquid of $\eta = 10 \text{ mPas}$ viscosity data can only be measured at the two highest rotor speeds, but these data could vary from about 9 to 11 mPas., i.e. the accuracy of the data is $\pm 10 \%$. For a liquid of $\eta = 10\,000 \text{ mPas}$ only the three lowest rotor speed values provide viscosity data, since higher speeds would provide excess torques against which the viscometer is electronically protected by an automatic motor overload cut-out.

SVDIN: Liquids of $\eta = 10 \text{ mPas}$ do not provide any significant viscosity data. For a liquid of $\eta = 100 \text{ mPas}$ the three highest rotor speeds allow viscosity measurements but only the data at the rotor speed of 600 1/min are accurate within 5 %. On the other hand this package of viscometer and this sensor system allows to measure viscosity data for liquids in the 100 000 mPas range.

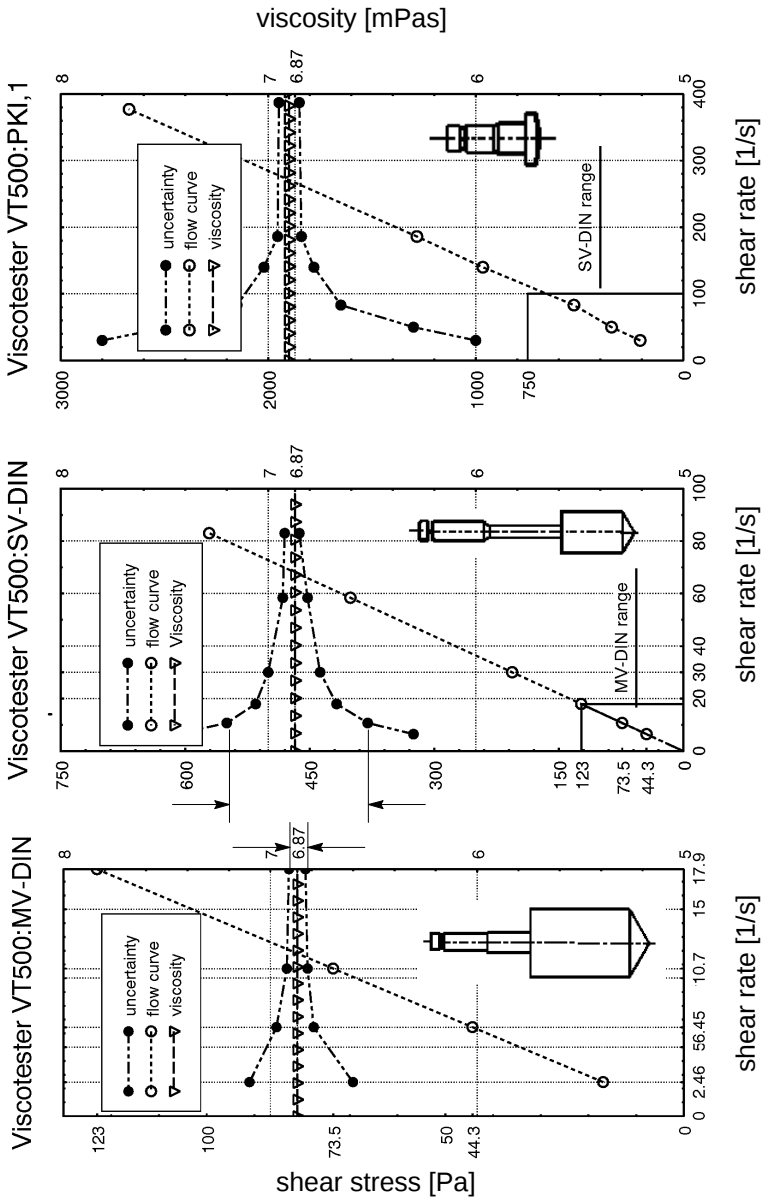


Fig. 98 Comparison of several sensor systems related to their test accuracy as indicated by their trumpet curves

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Fig. 98 plots the flow- and viscosity curves of tests with two similar coaxial cylinder systems and one cone/plate sensor system: MVDIN, SVDIN and PK1, 1°, which differ in their shear stress range. Their silhouettes are shown above in correct proportion to each other. The measured test points of the flow curve are circle-marked. The MVDIN can not be used for shear rates beyond $\dot{\gamma} = 17.9$ 1/s, the SVDIN not beyond $\dot{\gamma} = 83$ 1/s, while the PK1, 1° extends the shear rate up to $\dot{\gamma} = 400$ 1/s. This is in line with the shear rate factors A: the value A of the MVDIN is about 3.5% of the one of the PK1, 1°. All 3 sensor systems were tested with the identical Newtonian liquid of $\eta = 6.87$ Pas and this leads to identical viscosity curves parallel to the abscissa. The tolerance ranges of the tables in Fig. 98 were additionally introduced as trumpet curves around the viscosity curves to optically indicate those shear rates which provide acceptable levels of viscosity accuracy.

The conclusion of Fig. 98 is: If accurate data is required at low shear rates, the larger MVDIN sensor system is the best choice with viscosity data of the highest significance. It cannot provide any data at high shear rates. These can be realized by sensor systems providing a very much smaller shearing surface as is the case of the small size cone PK1, 1°. It provides good viscosity data at shear rates up to $\dot{\gamma} = 400$ 1/s but its low shear rate data is virtually of no use: At $\dot{\gamma} = 10.7$ 1/s, the value τ is only 2,5% of the full scale and it is accordingly insignificant. Whenever viscosity data is reported, their relevant levels of significance must be omitted.

6.2.6 There is no simple answer to the question: How accurate are rotational viscometers?

The combination of a rheometer/viscometer with the chosen sensor system provides for a sample of a given viscosity a limited rotor speed range for which the viscosity data are guaranteed for an accuracy better than $\pm 2\%$. Choosing rotor speeds too low and/or a totally unsuitable sensor system the chosen test conditions can provide – even with a very accurate viscometer/rheometer – viscosity data inaccurate within a 30 to 50% range.

It is up to the **user** of these rheological instruments who has to choose suitable test conditions. If he wants high accuracy data for a given sample at low shear rates then he must choose sensors with small A-factors which provide a high sensitivity within a small shear stress range. If the relevant shear rates are estimated to be much higher then a new test must be run with a sensor system of smaller surface area and much larger A-factor. This will allow going to higher shear rates with an acceptable accuracy for the viscosity data, but the low rotor speed data will be inaccurate.

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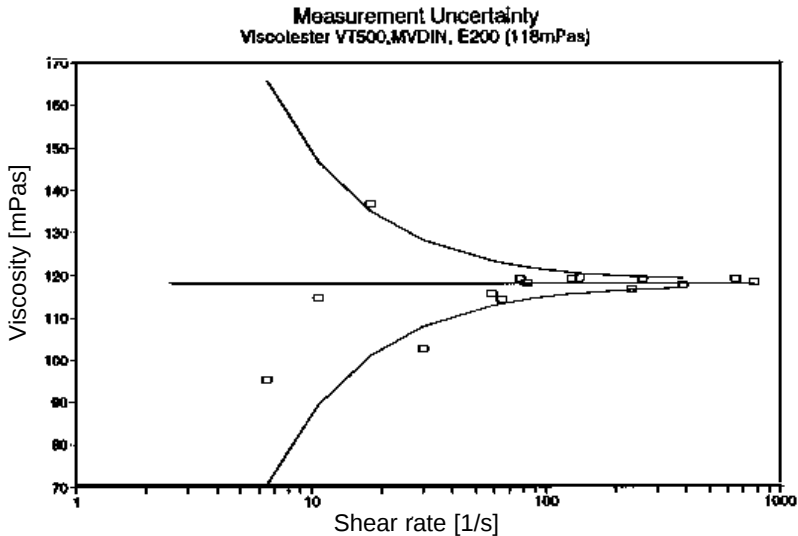


Fig. 99 Accuracy trumpet curve for a particular sensor system and fluctuation of viscosity data points dependent on shear rate.

Fig. 99 exemplifies such a test again with the Viscotester VT500 and the sensor system MVDIN used for the measurement of a calibration oil with a viscosity of $\eta = 118$ mPas at 20°C. The test points resulting from the individually chosen rotor speeds are indicated by the open squares. The total tolerance range specified for this viscometer package around the viscosity curve being a parallel to the abscissa is indicated by the trumpet shaped lines. It is obvious that choosing shear rates $\dot{\gamma} < 100$ 1/s provide viscosity data which are questionable.

Under the condition that viscosity data must provide an accuracy of better than 2-3 % then any particular package of viscometer/rheometer will cover only about a decade of shear rate.

If several decades of shear rate must be precisely covered, several tests with different combinations of viscometers/rheometers and sensor systems are required. Thus the manufacturers of rotational rheometers provide a modular system of interchangeable sensor systems – coaxial cylinder-, cone-and-plate-, and parallel-plate – which differ in shape, active surface area and in their gap sizes.

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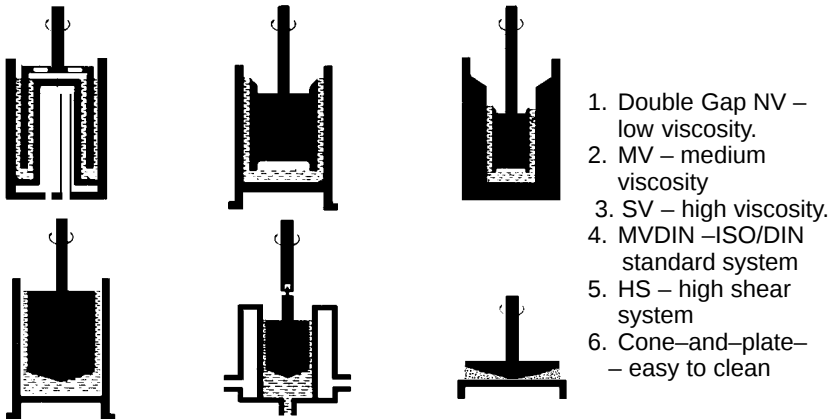


Fig. 100 Six typical sensor systems out of thirty which may be used with a HAAKE Viscotester VT550 differing in gap size and active surface on the rotors.

“Playing” with the sensor systems that are available, one can choose a sensor system which offers a large active shear surface for the viscosity measurement of a low viscous lotion: i.e. the HAAKE double-gap system NV and the shear stress factor $A = 363 \rightarrow \tau = 0-73 \text{ Pa}$ for a viscometer VT550. If a bitumen with a very high viscosity is tested then one will look for a sensor with a small surface area to keep the resulting torque within the reach of the viscometer: i.e. a cone-and-plate sensor system HAAKE PK2 rated with a factor $A = 47750 \rightarrow \tau = 0 - 10000 \text{ Pa}$ – see equation [14]. The exchange just of the modular sensor systems expands the shear stress range by more than 2 decades.

If the assessment of the shear rates in production or usage indicates that one needs results at low shear rates then one will use sensor systems of large gap sizes with a small shear rate factor M : i.e. the HAAKE SV1 with $M = 8.9$ – see equation [12] – which provides for a rotor speed $n = 0.5-800 \text{ 1/min}$ a shear rate range of $\dot{\gamma} = 0.45 - 712 \text{ 1/s}$. Choosing alternatively a HAAKE “high shear” HS1-system with a $M = 400$ and a gap size as low as 25 microns raises the maximum shear rate to $\dot{\gamma} = 32\,000 \text{ 1/s}$. The ratio of the M -factors is 1:44.5. Since this viscometer makes use of a step-motor speed control its assigned rotor speeds are very accurate even at the low speed end. The tolerance range of the shear rate is therefore more linked to the geometry accuracy than to the one of speed. It is safe to assume that the instrument package of viscometer and sensor system maintains the shear rate accuracy to better than 1%.

The scope of testing with rotational rheometers/viscometers can be still further extended by selecting rheometers which have much extended shear stress-

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and shear rate ranges: CS-rheometers can measure solids below their yield value and liquids almost as low viscous as water at room temperature.

Please note:

below $\eta = 2$ mPas Ubbelohde capillary or falling ball viscometers are a better choice than almost all even otherwise top-class rotational rheometers because they are in this viscosity range more accurate – and even lower priced.

Choosing the right sensor systems involves often further criteria such as filling higher viscous sample into small gap sizes, avoiding pre-shear for thixotropic samples, obtaining reasonable results for heterogeneous samples with large particles such as in orange marmalade etc.

The above will have made it clear that it is an important task for the user to select the optimum rheometer/viscometer for a given application. A major consideration should always be the accuracy that can be attained with a particular instrument package, the choice of the relevant shear rates and practical thoughts of how to fill a sample undisturbed into a sensor and how to clean afterwards. Combining all these thoughts requires experience gained in weeks, months or even years.

An operator cannot do much in laboratories with a wide range of samples even with a sophisticated rheometer if the choice of sensor systems is limited to e.g. two types of cones and one lower plate.

In comparison to glass Ubbelohde capillary viscometers or Hoeppler falling ball viscometers, the viscosity measurements of rotational rheometers are less accurate especially for low viscosity liquids. But inasmuch as the rotational rheometers are so much more versatile, users will still choose them to solve all kinds of rheological problems related to non-Newtonian, visco-elastic fluids for which those other viscometers are just not suitable.

The above considerations should be kept in mind when calculating viscosity data by dividing the measured data of shear stresses by shear rates making use of modern calculators. Viscosity that is never measured – as the result of the mentioned, combined tolerance parameters – with a tolerance better than 2% and the test reports consequently must not be given as a 8-digit value. This can be pin-pointed by the following example taken from extruder capillary rheometry:

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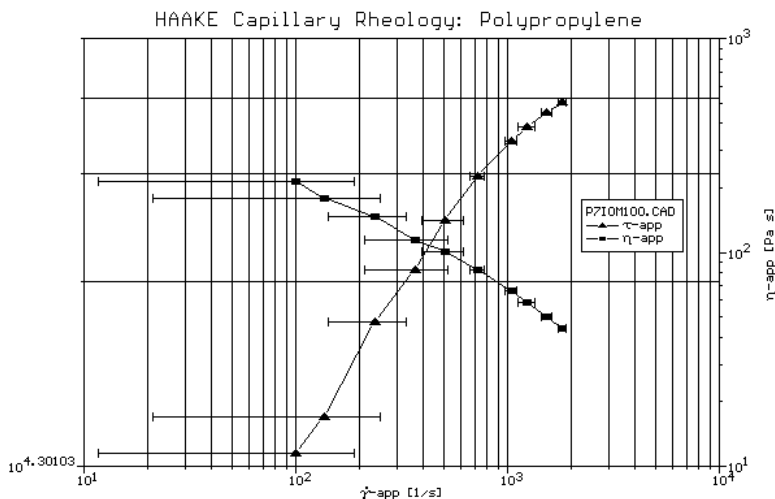


Fig. 101a Flow and viscosity curves showing “error bars”

Column	1	2	3	4	5	6
Quantity	$\dot{\gamma}$ -app	τ -app	η -app			
Format	significant	floating	significant	Exponent	Exponent	Exponent
File	P710M100.C	Exponent X.XXE+0Y				
Range	...	floating p. XXXXXXX.YY				
		significant digits XX				
	7.2E	Exponent X.XXE+0Y				
	1E	floating p. XXXXXXX.YYY				
	1.2E	significant digits XXX				
	1.5E					
	1.8E+03	78125		44		

$\dot{\gamma}$ -app [1/s]	τ -app [Pa]	η -app [Pa s]	$\dot{\gamma}$ -app [1/s]	τ -app [Pa]	η -app [Pa s]
99.224	20875	210.384	99	20875	2.1E+02
136.432	23937	175.453	1.4E+02	23937	1.8E+02
235.656	34250	145.339	2.4E+02	34250	1.5E+02
367.954	41625	113.126	3.7E+02	41625	1.1E+02
508.521	50250	98.816	5.1E+02	50250	99
719.371	59125	82.190	7.2E+02	59125	82
1033.578	67687	65.488	1E+03	67687	65
1240.294	71437	57.597	1.2E+03	71437	58
1529.696	75312	49.234	1.5E+03	75312	49
1794.292	78125	43.541	1.8E+03	78125	44

Fig. 101b Modern software allows operators to choose different forms of tabulated test results with up to 8 digits or just significant – columns 4 and 6 – data

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The tests which provided the flow- and viscosity curves of Fig. 101a were run with the instrument package as shown in Fig. 37. An extruder feeds molten polymer through the capillary rheometer die to produce a fibre-type extrudate. The pressure drop along the length of the capillary provides a pressure drop which relates to the shear stress. The extrudate feeds onto a balance, which provides for a given time span a flow rate value Q . It can be evaluated in terms of shear rate. When the flow of the polymer is not evened out by means such as a melt pump prior to the entrance into the capillary die, one must expect for fibre extrusion some fluctuations in the rate of flow, which are percentage-wise larger at low flow rates than at higher. This is detected by the computer to which the balance sends its signals. The computer checks the flow rate signals for a given time span, determines mean, minimum and maximum data and evaluates the related shear rate values, but it provides in addition the “error value = level of insignificance” for the shear rate. The length of the horizontal bars attached to the measuring points of the flow- and the viscosity curves in Fig. 101a indicates the insignificance of the data points especially at low shear rates rendering the two lowest test points almost useless. The additional feature of the “error bars” which can be inserted or omitted provides in the diagrams additional important information on the relevance of the test results which the flow- or the viscosity curves alone do not provide. The curves above are just indicated with their shear rate error bars, but this should not be understood as meaning that the pressure/shear stress data are not linked to tolerances as well. They are here omitted to prevent unnecessary confusion.

Seeing the error bars of Fig. 101a one should be induced to look for test conditions which are likely to result in smaller fluctuations of the flow rate: the use of a melt pump or different extruder screws with longer metering sections etc.

But Fig. 101b should also make operators aware of the following risk: Modern computer software may provide not only graphical but also tabulated results. The data of shear rate, of shear stress and of viscosity are the result of a mathematical transformation of the original, measured data such as flow rate and pressure drop. The original data such as the shear rate in this example possesses often only 1 or 2 significant digits. The computers will easily deliver the resulting values as in the table of Fig. 101b in 7 or even 8 digits but this can be considered “non-sense” on the background of the insignificance of the shear rate data at low shear rates.

Even under optimum test conditions capillary or rotational rheometers will not provide viscosity data for one decade of shear rate with more than 3 significant digits. The more digits beyond 3 are reported, the more the person responsible for presenting the data will indicate his incompetence!

6.3 Possible causes of misinterpretation of test results.

6.3.1 Maladjustment of “zero” on the shear stress scale.

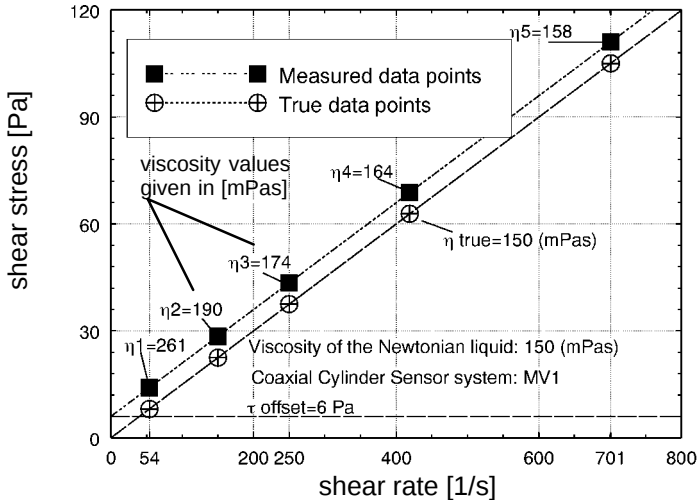


Fig. 102 Viscotester VT550: Effect of poor zeroing on the results of the measured viscosity

Fig. 102 shows a typical flow curve of a Newtonian sample which does not start from the origin of the diagram.

A correct flow curve of such a liquid is a straight line with a constant slope starting from the origin – dashed line with true data points (cross-circle points). The measured flow curve (square points) appears as a parallel shift to the correct flow curve by “only” some 5% upwards on the shear stress ordinate. When calculating the ratios of shear stresses and shear rates for the measured data points variable values of η are found which differ by more than 40 % from the true viscosity value. These calculated viscosity data appear to be dependent on the shear rate, which attributes a non-Newtonian flow behavior to a liquid which is in fact Newtonian. A small error in the zero-adjustment leads to calculated viscosity values especially for low values of shear rate which are strongly erroneous!

It is evident that a correct zeroing is most important. Modern computerized rheometers allow an automatic zeroing prior to the start of the actual test.

In this context, a very practical advice might be helpful:

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When testing fluids possessing strong yield values making use of CR-viscometers with spring-type torque sensors, zero the instrument **before** filling the sensor system.

Filling then the sensor system with the test fluid will cause inevitably some zero-offset of the torque signal at rotor stand-still. This is caused by the yield point of the sample which prevents the torque sensor having been deflected during filling to fully release its tension and thus does not allow the torque/shear stress signal to return to zero. One should **not re-zero** the instrument again but instead one should start now the test and plot the flow curve. When the shear rate increases lead to stresses beyond the yield value the rotor will be free to rotate and the sample will start to flow with the resulting torque signals being correct.

6.3.2 The effect of excess sample volumes.

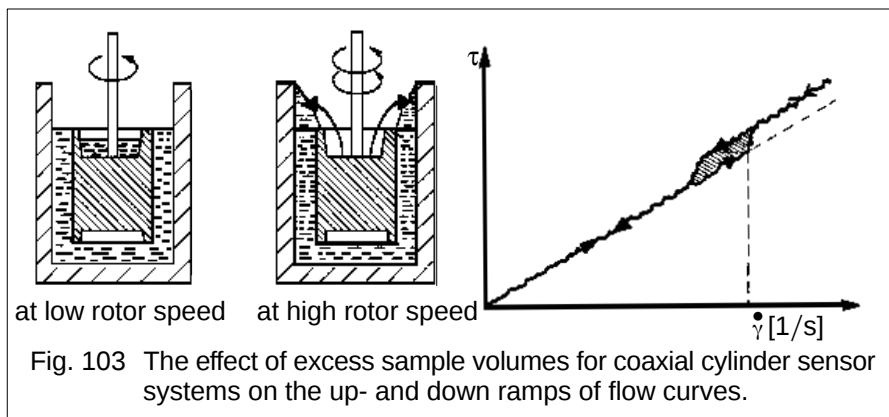


Fig. 103 The effect of excess sample volumes for coaxial cylinder sensor systems on the up- and down ramps of flow curves.

End effects for coaxial cylinder sensor systems used in Searle type viscometers can introduce sizable errors. The traditional HAAKE design of rotors eliminates those effects with rotors which are recessed on the bottom and on the top. If the sample volume introduced into the measuring gap was too large, some sample will overflow into the upper recess. This keeps the gap well filled up to the upper rim of the rotor and thus allows a correct measurement of shear stress and viscosity. The excess sample will add to the weight and inertia of the rotor but this effect is negligible. Problems arise and an error is introduced at high rotor speeds when the resulting centrifugal force throws the excess sample out of the upper recess onto the wall of the outer cylinder causing it then to be additionally sheared thus adding stepwise to the measured torque. The flow curve will in such a case show a stepped-up shear stress signal and an hysteresis when the flow curve is determined with ramps of increasing and decreasing shear rates – Fig.103.

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The lower end face of the rotor being recessed allows to keep it air-filled when pushing the cup with the sample upwards during the filling of the sensor system. When rotating the rotor during the test, most of its end face effect – additional torque signal – is related to the very low viscosity air being sheared in the lower recess and this effect can again be neglected.

This design of the recess in the bottom of the rotor is very good for constant temperature viscosity tests. If tests are run with programmed temperature increases or decreases the expansion or contraction of the air encapsulated in the recess will cause problems. Then ISO/DIN-type rotors with their conical end faces are a better choice.

When making use of ISO/DIN-type sensor systems which are designed with a flat top end, one should also avoid much overfilling. This excess sample will in the case of a programmed shear rate increase gradually be subjected to the centrifugal forces with the result that more and more of the excess sample will contribute to the measured shear stress.

Conclusion: When working with recessed and ISO/DIN-type rotors one should be careful with the introduced sample volume. If excess sample did get into the upper recess of a rotor or much above the upper face of a ISO/DIN-rotor, it is a good procedure to suck most of the excess sample out by means of a syringe or a pipette.

6.3.3 The effect of damping on flow- and viscosity curves.

There are samples that are very heterogeneous such as human sputum. Testing them rheologically in a CR-viscometer will produce at fixed shear rates wide fluctuations in the measured shear stress as a function of time. If such a viscometer is equipped with means to electronically or mechanically dampen the torque signal it makes sense in such a case to use this damping. It will provide a mean stress signal constant with time. Sputum flow curves are then best determined stepwise at different constant shear rate values.

Damping in almost all other cases is negative in rheometry, because it is likely to introduce a time-dependent error, which can be large and lead to wrong conclusions for the evaluated results.

Some damping may be inevitable. CS-rheometers are damped by the inertia of large and heavy rotors and some inertia is always related to the design of its measuring system.

Computerized CR-rheometers allow a programmed shear rate ramp program – CS-rheometers have a similar stress ramp program –, which allows one to automatically increase the shear rate from low to high values and back again. One can also choose the rate – acceleration – for this ramp. Torque sensors which are damped will show a time-lag between the assigned shear rate and the resulting shear stress. If the ramp rate is high, the shear rate is attained before its shear stress counterpart has been achieved.

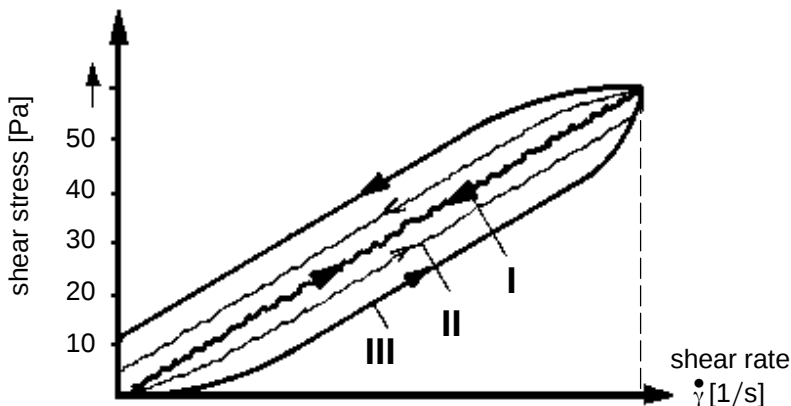


Fig. 104 Instrument damping or a high rotor acceleration during tests of high viscosity fluids can result in a counter-clockwise hysteresis of flow curves

A schematic flow curve diagram (Fig.104) is used to demonstrate the effect of damping: an ideal Newtonian flow curve I will be straight and the curve of the up-ramp will fall on top of the down-ramp curve under the condition that the ramp rate is low. Increasing this rate will provide the up- and down hysteresis curves No.II: it is a looped curve with a counter-clockwise direction and the stress values related to any shear rate are below the true values for the up-ramp and higher for the down-ramp.

The higher the viscosity of a liquid – internal damping of the sample –, the higher the damping of the torque sensor – instrument damping –, and the higher the rate of ramp rate is, the wider is the hysteresis loop as pointed out in curve No.III.

Viscosity data of high accuracy require that an equilibrium condition between the assigned shear rate and the resulting shear stress – or vice versa – is attained before test conditions are again altered. If a test is programmed with a shear rate ramp, any instrument damping must be cut out and the ramp rate must be optimized.

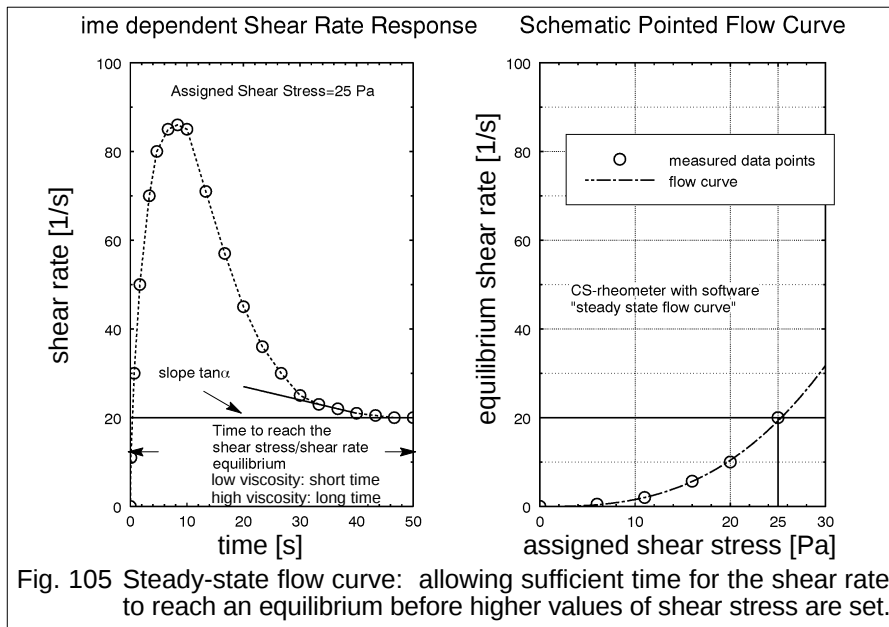
Ramping was invented to automate the plotting of continuous flow- and viscosity curves and thus it may save operator time, but when not carefully used, ramping can lead to errors in the magnitude of 10 to 20%.

Modern computer software for rheometers allows to eliminate the danger of damping on test results by providing an alternative to the shear rate or stress ramping: plotting “steady state” flow curves is demonstrated for a CS-rheometer

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– Fig. 105. This computer program measures flow- and viscosity curve within a preset shear stress range. The assigned shear stress values – normal are 10–20 – are automatically preset in ascending steps one after the other, but the next higher step is only initiated after the equilibrium value of the resulting shear rate value has been reached.



A sub-window on the computer screen plots for any assigned shear stress value the resulting shear rate as function of time. Whenever the next higher shear stress value is assigned the resulting shear rate will initially peak. It will then take some time until for visco-elastic samples the shear rate/time-curve coming down will establish on its true equilibrium level. The software provides limit default values which allow one to raise the shear stress to the next higher level only after:

Please note: for thixotropic samples the shear rate/time curve will approach the equilibrium value asymptotically **from below**, i.e. when the sol-status of the liquid has been reached.

a.) the slope of the shear rate/time curve has dropped below a preset level – ideally a change less than 0.01%.

b.) a given time-span has ended, which in previous tests with a particular sample was found to be sufficiently long to reach the required rheological equilibrium.

The “steady-state” flow curve program especially with limit default a.) takes care automatically of the need to wait longer to reach the shear rate equilibrium for

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higher viscous samples. The price of the much improved flow curve accuracy is increased testing-time: perhaps 10 min or more, while the stress ramping program may already provide – less accurate – data within two to three minutes.

6.3.4 The effect of frictional shear heat on viscosity data.

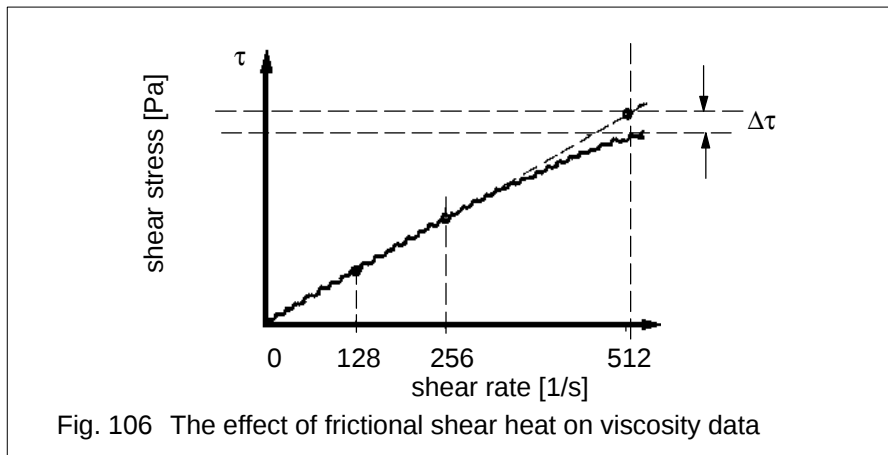


Fig. 106 shows again schematically a typical CR- flow curve of a Newtonian liquid, which clearly deviates from the expected theoretical straight line flow curve in the upper third of the shear rate range. It is well known that the viscosity of all liquids and especially of mineral oils is greatly dependent on temperature. Most oils, polymer melts or solutions, greases and the like are also poor heat conductors. If these viscous substances are subjected to high shear conditions the shear energy is transformed into frictional heat raising the sample's temperature. This frictional heat cannot be conducted rapidly to the outside metal walls of the thermostated coaxial cylinder- or cone-and-plate-sensor systems. More heat is produced inside of the sample than can possibly be removed per time unit by means of any connected thermal liquid thermostat or Peltier-element cooling. The temperature of a highly sheared sample will often be found to have increased 2, 3 or even 10°C above the preset temperature level. Considering the fact that often a 1°C temperature increase can easily mean a 10% decrease of viscosity, an unnoticed shear heating will result in a decrease of the accuracy of viscosity data rendering them useless.

Shear heating as such cannot be avoided even by the most elaborate method of cooling any sensor system. If one cannot limit the shear rates, one can reduce the effect of shear heating due to high shear testing: A continuous ramping of the assigned shear stress or shear rate will mean that increasing with time more shear heat is accumulated in liquid samples of often small volume and the mass temperature will consequently increase strongly.

Programming the test alternatively with stepped-up shear stress/shear rate values and allowing between each level of shear stress/shear rate a sufficient time period at rotor stand-still, this procedure will allow the removal of accumulated shear heat. Again an increase of testing-time is the price for maintaining a sufficient accuracy of the high shear test data! Fortunately computer programming can at least keep operator involvement minimal.

6.3.5 The effect of insufficient time to reach any assigned temperature level

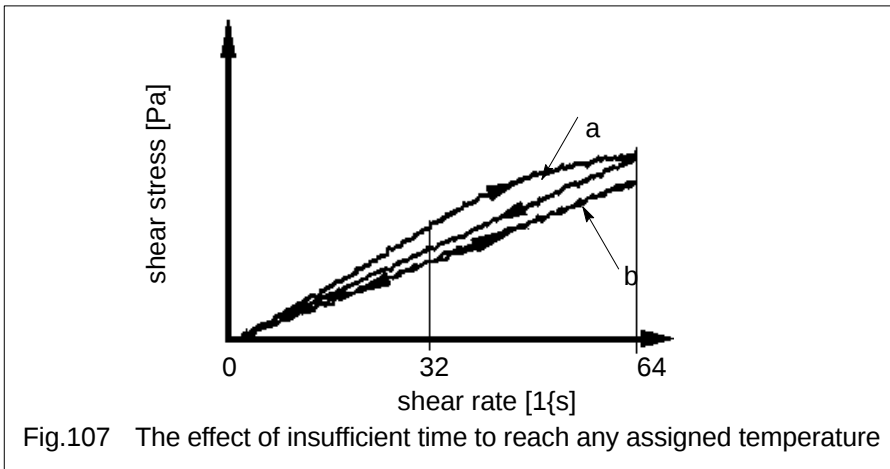


Fig.107 The effect of insufficient time to reach any assigned temperature

The CR-flow curves of Fig. 107 were the result of a test procedure as described in the following:

A sample of a bitumen of high viscosity and poor heat conductivity was to be tested at a temperature of 140°C making use of a sensor system MVDIN. Most unblended bitumens can be assumed to show a near-Newtonian flow behavior, i.e. their viscosity is almost independent of the shear rate. The sample having been preheated to a temperature of 120°C to allow pouring it into the gap of the coaxial sensor system was then tested immediately under the assumption that it would “in no time” acquire the temperature of the sensor systems preheated to 140°C. The up- and down ramp program was preset to total some 5 min: it resulted in a looped hysteresis flow curve a.) with the “up-curve” being above the “down-curve”. Repeating the same ramp program a second time provided the linear curve b.) with the superimposed up- and down-ramp curve segments.

A bitumen is normally non-thixotropic and this leads to the assumption that the difference between the a.) and b.) curves can be explained as the result of an

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insufficient pre-warming period, i.e. the test a.) was already started before the sample had reached the assigned temperature. When the second test cycle b.) was started, 5 more minutes had been allowed for the first cycle during which the sample was still further heated from the outside and by frictional heat from inside. One can conclude that only the test cycle b.) gave an acceptable test result.

Operators have to keep in mind that reaching an assigned temperature will always take some time – sometimes seconds but more often several minutes depending on the chosen type of the sensor system and its gap size, on the level of the assigned temperature and the heat conductivity of the test sample. Only preliminary tests for a family of samples will indicate how long the pre-warming period has to be in order to ensure an acceptable accuracy of the test data.

It is a valuable feature of modern computer software that the actual rheological test does not start until the actual temperature of the sample – measured by means of a temperature probe installed for instance in the lower plate of a cone-and-plate sensor system – is within 0.1 or 0.2°C of the assigned temperature.

6.3.6 Effect of chemical or physical changes in tested samples

One of the “boundary conditions” – chapter 2.9 – for good rheometry was that conditions should be avoided which provide both variable shear rates and chemical and/or physical changes at the same time.

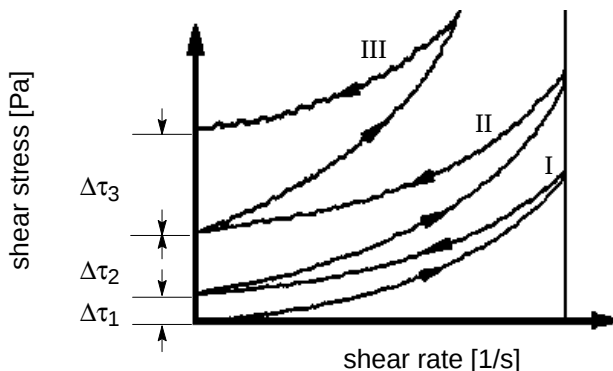


Fig. 108 The effect of chemical or physical changes on the viscosity of the tested sample

Test results as indicated in Fig. 108 offended these boundary requirements:

The test sample was a PVC-plastisol, which is a suspension of emulsion-type PVC-particles in a liquid plasticizer. This plasticizer just fills the voids between

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the PVC-particles rendering the suspension to be a highly viscous, heterogeneous fluid, which is known to show a dilatant flow behavior. At higher temperatures the PVC-plastisol can gel, which means that the plasticizer penetrates into the PVC-particles with the result that the plastisol changes into a more or less homogeneous, much more viscous mass.

Flow curve No. I shows in the first up-ramp normal dilatant flow behavior. The down-ramp is not superimposed on the first segment but instead reaches the ordinate at a shear stress level $\Delta\tau_1$ above the origin. Such a counter-clockwise loop could remind people of rheopectic flow behavior, which is anyway more than rare and which definitely does not describe PVC-plastisol behavior. This is verified when this test is repeated for a second or third cycle with the same plastisol sample providing new flow curve loops No. II and III with the hysteresis increasing with each new cycle.

This unusual flow behavior is the result of accumulated shear heat causing the start of a gelation by which the plastisol changes its physical composition and its PVC-particle- and plasticizer interaction.

Whenever chemical – gelling, curing, or hardening – or physical processes – solvent loss, or particle sedimentation, etc. – take place, the operator must be aware of such disturbing effects unless his aim is to just monitor these processes.

6.3.7 The effect of non-laminar flow

Testing Newtonian liquids of very low viscosity such as water in a Searle-type rheometer/viscometer can lead to a flow curve as schematically pictured in Fig. 109:

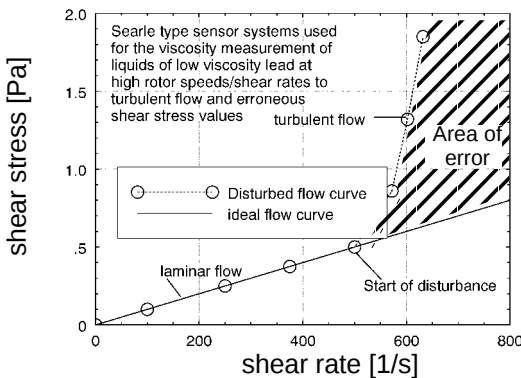


Fig. 109 Searle type sensor system: The effect of the transformation of laminar to turbulent flow on a flow curve of a Newtonian liquid.

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At low and medium shear rates the flow curve is linear as expected, but at high shear rates the curve drastically breaks away from the linear pattern. In this part of the flow curve the shaded area between the measured flow curve and the theoretical, linearly continuing curve indicates the amount of additional shear energy that has gone additionally into the sample to maintain a non-laminar flow. The non-linear shear stress increase for a linear shear rate ramp is caused by a transformation of the linear to a turbulent flow pattern. Under the heading of the “boundary conditions” a non-laminar flow was excluded whenever test results were to be evaluated in terms of absolute viscometry. Thus turbulence can be considered a disturbance, which causes grave errors – 20 to 30 % or even more – in viscosity test results whenever unsuitable test conditions are chosen and remain unnoticed.

Such a transformation of laminar to non-laminar flow is linked to a Searle-type design of sensor systems of rotational rheometers: – the rotor rotates and the outer cylinder is fixed. The testing of low viscosity liquids at high shear rates can lead in Searle-type sensor systems to vortices and turbulence in the sample. They are caused by the combined action of circumferential- and centrifugal forces acting on liquid volume elements:

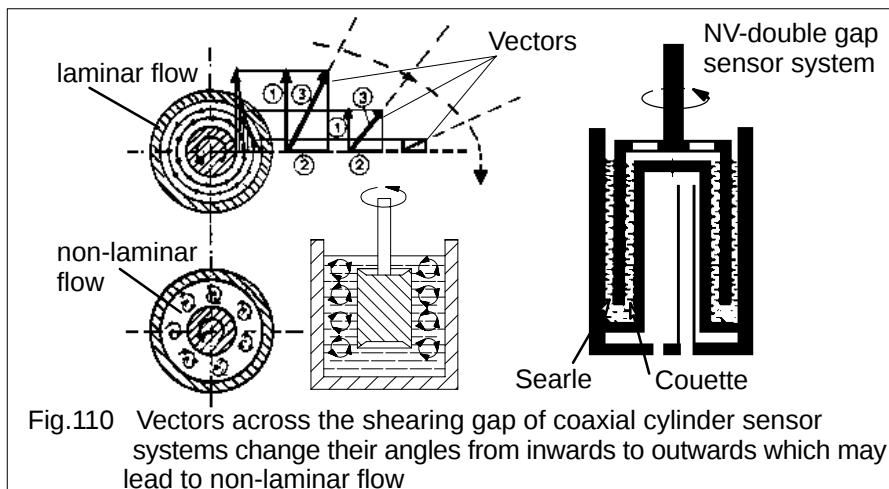


Fig. 110 indicates the forces which act on volume elements taken at 3 different points across the gap of a coaxial cylinder sensor system. The tangential forces (1) decrease from a maximum near the rotor surface. The centrifugal force (2) is reduced for volume elements placed at positions with increasing radius. Circumferential and centrifugal forces always combine on each volume element to form a resultant force, (3) which changes its vector angle and size across the gap. This may initiate a secondary cycled flow in the annular gap

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leading to vortices whenever criteria of the so-called Taylor-numbers or limits have been surpassed, which are related to both the flow speed and the kinematic viscosity of the tested sample.

It is worthwhile mentioning that Couette-type rheometers do not show such a non-laminar flow pattern:

In Couette type sensor systems the outer cylinder rotates, while the inner cylinder/rotor is used to determine the resulting torque. A volume element rotating close to the outer cylinder is subjected to the highest circumferential speed. But it can not move outwards as the result of the centrifugal force acting on it, because obviously it cannot enter into the metal cylinder wall of the outer cup. Any other volume element further inwards in the annular gap is also prevented to move outwards: it would have to displace other volume elements still further outwards, which also cannot give way in the radial direction. With the effect of the centrifugal force to initiate any radial vector thus eliminated, vortices and non-laminar flow do not occur in Couette-type rheometers.

Please note: Searle type rheometer combined with double-gap sensors systems – HAAKE nomenclature: NV – have a Searle-type gap in the outer gap but additionally a Couette type gap on the inside of the rotor. With such a NV-sensor system one can also run into the non-laminar disturbance for low viscosity liquids tested at high shear rates. Operators should be aware of this possibility and the large errors that can be connected with it.

6.3.8 The influence of the gap size on the accuracy of viscosity data

In the chapter Quality Criteria for Coaxial Cylinder Sensor Systems (pages 51-53) it has already been pointed out, that the gap size of the chosen sensor has a very strong influence on the accuracy of the viscosity data of a non-Newtonian fluid. The smaller the gap size is, i.e. the more the ratio $\delta = R_a/R_i$ approaches the value 1.00, the more accurate these values will be. For a given rotor speed n (1/min), the shear rate at a rotor radius varies with a factor dependent on the ratio of the radii:

$$\begin{aligned}\text{The given example was: } \delta = 1.01 &\rightarrow \dot{\gamma} = 10.6 \cdot n \\ \delta = 1.10 &\rightarrow \dot{\gamma} = 1.10 \cdot n \\ \delta = \text{infinity} &= \dot{\gamma} = 0.105 \cdot n\end{aligned}$$

For the adhesive sample tested in sensor systems defined by the above values δ and the same rotor speed, the measured viscosities were:

$$\begin{aligned}\eta_1 &= 6.78 \text{ mPas} \rightarrow 100\% \\ \eta_2 &= 10.72 \text{ mPas} \rightarrow 158\% \text{ of } \eta_1 \\ \eta_3 &= 19.0 \text{ mPas} \rightarrow 280\% \text{ of } \eta_1\end{aligned}$$

The value η_1 can be assumed to come closest to the true viscosity of the sample. For the viscosity measurement of Newtonian liquids all coaxial sensor systems of different ratio δ and even a single rotor in a very large container will give identical viscosity data. Inasmuch as in normal quality control of fluids the number of non-Newtonian samples will far exceed those of oils, the right choice of the sensor system is of high importance for the accuracy of viscosity data of suspensions, dispersions, polymer melt etc.

6.3.9 The influence of gap size on phase separation in dispersions

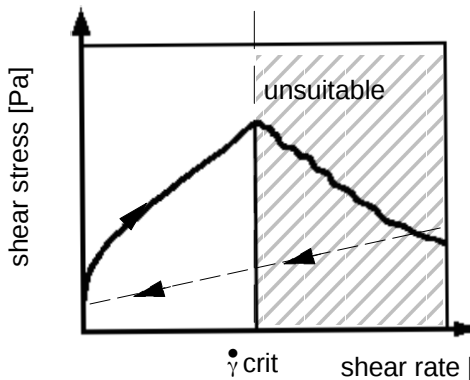
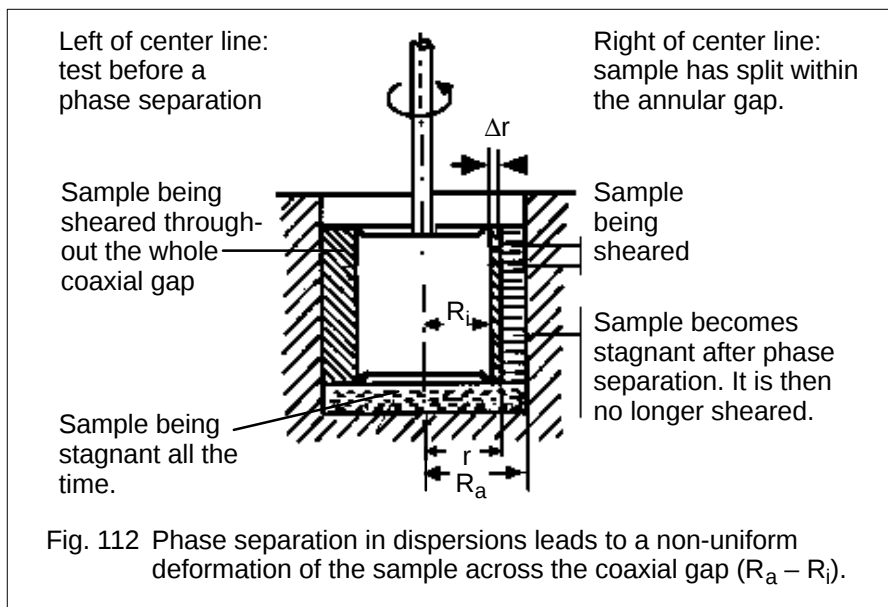


Fig. 111 Increasing shear rates beyond critical levels provides faulty viscosity data on dispersions which can show phase separation.

In dispersions, such as tooth paste or clay/water compounds, with a high concentration of filler particles well mixed with a liquid to form a paste, testing can lead to a flow curve of a CR-viscometer test as shown in Fig. 111. Increasing the shear rate starting from zero with a ramp program provides most of the time an initial stepwise increase in the resulting shear stress – indication of a yield value – and then a further gradual stress increase. At a critical shear rate level $\dot{\gamma}_{crit}$ the curve starts to strongly deviate from the previous, upwards sloping pattern. The curve instead dips-down for further increased values of shear rate to almost zero-stress-levels. If one would ramp the shear rate down again, the flow curve will not follow the curve of the up-ramp but “crawl” back to zero shear rate at a lower stress level.

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The flow curve beyond the level $\dot{\gamma}_{crit}$ must be considered as faulty and its evaluation will lead to rheologically useless results. One may assume (see Fig. 112) that in such a case at a given critical shear rate the tested paste will split into a thin liquid layer at the rotor surface while the remainder of the sample in the annular gap becomes stagnant. In fact it means that under these conditions the geometry of the annular gap is in effect drastically changed. Only the small fraction of the sample close to the rotor containing almost only the fluid component is still being sheared in a newly formed coaxial cylinder gap of unknown gap size. This liquid layer being low viscous leads to low values of resulting shear stresses and thus the drop of the flow curve at high shear rates. Once the sample has separated into the stagnant mass further outwards and the thin layer near the rotor, it will never rejoin the whole mass again in a downwards directed shear rate ramp. Having discovered this disturbance effect by the broken flow curve pattern, one must limit further tests to shear rate values below the $\dot{\gamma}_{crit}$.

Whenever a flow curve abruptly discontinues from a gradual increase, it is a good reason to assume a disturbance.

6.3.10 Disturbances caused by testing visco-elastic samples in coaxial cylinder- or cone-and-plate sensor systems.

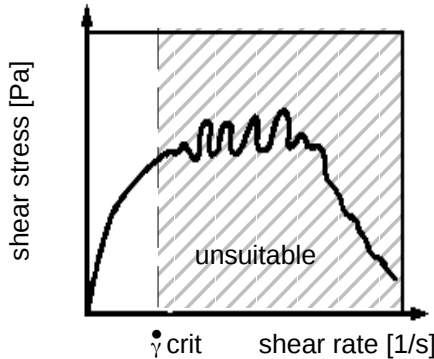


Fig. 113 A visco-elastic behavior of samples can lead to the Weissenberg effect causing faulty viscosity data beyond a critical shear rate $\dot{\gamma}_{crit}$

Fig. 113 optically marks a CR- flow curve which initially looks similar to a normal flow curve of a non-Newtonian fluid, but which from a critical shear rate onwards starts to strongly fluctuate and then to drop.

Very many polymer melts, solutions, and doughlike substances are increasingly elastic when shear rates become high. This causes the so-called "Weissenberg-effect": increasing shear rates lead to both increasing shear stresses **and** to normal stresses which eventually will even surmount the shear stresses. When this happens the normal force will create unstable conditions in the sheared sample and finally "force" the sample out of the shearing gap. With the gap of the sensor system remaining only partly filled, the shear stress signal is no longer meaningful. Beyond the $\dot{\gamma}_{crit}$ the flow curve cannot be evaluated anymore.

In order to retard the occurrence of the elasticity related disturbance on ramped shear rate programs, i.e. measure meaningful viscosity data at higher shear rates, one might try sensor systems with much smaller values of δ or smaller cone angles under the condition that particle sizes in the sample will allow this. In an open sensor system the emptying of the gap cannot be avoided as such but one can only shift its occurrence to higher shear rates with more suitable sensor systems.

Operators will have to keep an eye on the shape of the flow curve and on the rotors of sensor systems to inspect whether some of the sample has been drawn out of the annular gap or whether it is starting to crawl around the rim of a cone.

6.3.11 Decreasing the effect of solvent loss and particle sedimentation in dispersions

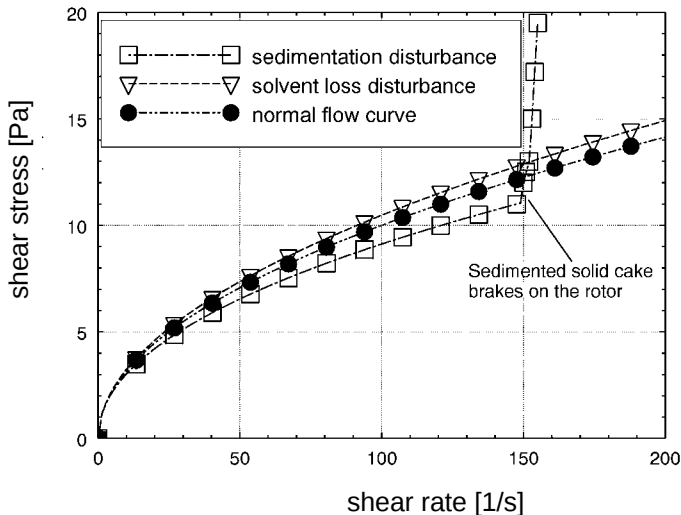


Fig. 114 The effect of solvent loss and of particle sedimentation causing faulty viscosity data of tested dispersions.

Many fluids are dispersions containing a continuous liquid phase that can evaporate at room temperature but even more so at elevated temperatures. Evaporation decreases the percentage of the liquid phase at a given temperature, thus gradually changes the composition of the fluid and it will result in a time-related viscosity increase (see Fig. 114: open triangles). Unless evaporation is counteracted by suitable means these viscosity data become dependent on a variable of unknown magnitude and they must be considered highly doubtful. This becomes even worse when solvent loss leads to a skin-forming on the sample surface open to the outside which “somehow” links rotor and cup or cone and plate.

There are a number of technical solutions which can be used to minimize or totally reduce solvent loss:

- decrease the open surface of the sample to the open air, by selecting sensor systems with a small annular gap size, i.e. coaxial cylinder sensor systems with a small ratio δ or cone-and-plate sensor systems with small cone angles.
- Minimize the effect of solvent loss for coaxial cylinder sensor systems by a reasonable overfilling above the upper end of the rotor. This excess sample

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will for some time provide some kind of a “lid” over the actual shearing gap and the sample in that annular gap. Loss of solvent from the surface of the excess sample has a of minor effect on the shear stress or viscosity data, since the excess sample sheared in the wide gap layer between the outer cup and the thin rotor shaft is subjected to a negligible additional shear rate and shear stress. At high rotor speeds overfilling (as it has been mentioned above) should be avoided.

Please note: Overfilling of cone-and-plate- or parallel-plate sensor systems to counteract solvent loss is no reasonable solution, because this adds to the active radius of the system which as cubed-radius influences the shear stress and the viscosity: even minor overfilling can have quite an effect on the accuracy of the viscosity data.

c.) Especially cone-and-plate- and parallel-plate sensor systems may be equipped with a doomed cover placed over them – often called “solvent trap” – made of glass that reduces free solvent loss. The initial solvent loss raises the partial pressure of the solvent gas in the space beneath the solvent trap and this reduces the rate of further solvent loss.

d.) If a solvent at ambient pressure but at elevated temperatures evaporates almost instantaneously then none of the above technical “compromises” will do. In order to allow a correct measurement of such dispersions a special sensor system must be chosen. The whole sensor system with the sample in place is housed in an autoclave that can be pressurized. A magnetic clutch transmits the torque provided by the rheometer/viscometer through a stainless steel membrane to rotate the rotor inside of the autoclave vessel. This very specially built sensor system can be designed to stand up to pressures of 20, 100 or even 1000 bars and they can make all the difference between good viscosity data or none for this group of solvent containing samples. Such a “pressure cell” is particularly important when measuring water-based suspensions and solutions above 100°C.

6.3.12 The effect of sedimentation of particles or corpuscles in dispersions

Many low viscosity dispersions such as low quality salad dressing or whole blood contain a sizable proportion of solid particles which may sediment if stored long-term in containers but also in the annular gap of coaxial sensor systems with the rotor at stand-still or at very low angular velocities. Sedimentation changes the composition of the sample and this results normally in a time-dependent viscosity decrease (see Fig. 114: curve with open square) in comparison to similar samples out of which particles cannot sediment (black dot flow curve). If all sedimented particles cluster at the bottom to form some kind of solid “cake”, this will eventually act as an additional brake on the rotor with the effect that the flow curve “shoots” upwards.

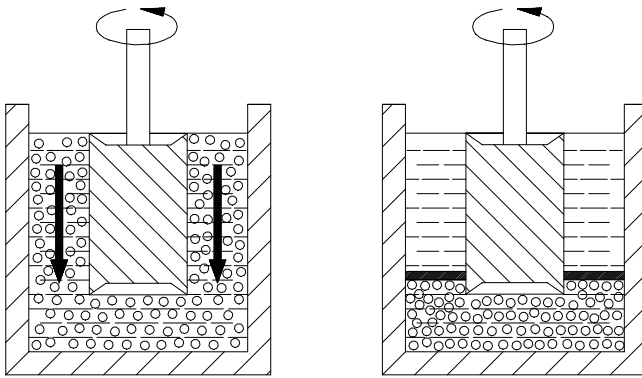


Fig. 115 Sedimentation of particles changes the homogeneity of dispersions and thus leads to a time-dependent change of viscosity data.

Sedimentation cannot be avoided as such but its effect on viscosity data may be minimized by the following procedure:

Instead of filling the sample into the annular gap, wait several minutes for the sample to reach the assigned temperature and then run a flow curve with the normal procedure starting from low to high assigned stresses/shear rates – some 5 to 10 min –, one can reverse this procedure: Immediately after filling the sensor the rotor speed increased in one step to the assigned upper limit. At this high speed the sample is warmed up more by frictional heat than by heat conduction from the jacketed outer cylinder so that the required test temperature can be attained much faster than leaving the sample at stand-still. At high speed the well known “hoola hoop effect” will prevent any particles from sedimenting. The rotor speed may then be ramped down rapidly so that the low speed range is transgressed within a short period of time and with almost no sedimentation. In whole blood viscosity testing it is a common procedure to maintain for 2 min a shear rate of $\dot{\gamma} = 200 \text{ 1/s}$. The measured shear stress at the end of this period can be converted to the viscosity value “ η_{200} ” related to $\dot{\gamma} = 200 \text{ 1/s}$. Then the shear rate is reduced in one step down to a constant shear rate of $\dot{\gamma} = 1 \text{ 1/s}$ for another minute. The resulting shear stress of this second phase is similarly converted to viscosity “ η_1 ”. These two viscosity data and their ratio are considered important for the medical evaluation of whole blood.

Having avoided in this reversed test procedure long pre-warming periods and sedimentation of red blood cells in plasma at a rotor stand-still, this test procedure will realistically determine the viscosity of whole blood at the low shear rate when red blood cells strongly aggregate and at the high shear rate when these corpuscular cells orient and form thimbles.

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Summary

It is hoped that the readers has not been frightened away from rheological testing after having read this chapter. A chemist or engineer not yet versed in the "tricks of the rheometry" cannot hope to unpack a new rheometer, pick a sensor system and minutes later measure meaningful results.

The **quality of the rheometer** is one side of the problem for getting highly accurate viscosity data that are meaningful within the context of a production procedure, a scientific screening of polymers for their molecular structure or a quality control problem.

An experienced **operator** will be at least as essential for the acquisition of good rheological data which are meaningful for scientific tasks or for quality control!

7. The Problem of Shear Heating

The following equations allow the calculation of shear heating and the resulting temperature rise.

Assumption: heat is neither transported into the sample from the outside nor lost to the outside.

The energy required to sustain flow in the annular gap of a rotational viscometer ends up as heat:

$$N = M_d \cdot \Omega$$

$$A = M_d \cdot \Omega \cdot t$$

$$N = \text{energy} [N \cdot m/s]$$

$$A = \text{work} [N \cdot m = J]$$

$$M_d = \text{torque} [N \cdot m], \text{ linearly related to the shear stress}$$

$$\Omega = \text{angular velocity} [s^{-1}], \text{ linearly related to the shear rate}$$

$$M_d = 2\pi \cdot h \cdot R_i^2 \cdot \tau$$

$$\Omega = \frac{R_a^2 - R_i^2}{2 \cdot R_a^2} \cdot \dot{\gamma}$$

$$N = \pi (R_a^2 - R_i^2) h \cdot \frac{R_i^2}{R_a^2} \cdot \dot{\gamma} \cdot \tau$$

$$V_s = \pi (R_a^2 - R_i^2) h$$

$$V_s = \text{sample volume in the annular gap} [cm^3]$$

$$N = V_s \cdot \frac{R_i^2}{R_a^2} \cdot \dot{\gamma} \cdot \tau = V_s \cdot \frac{1}{\delta^2} \dot{\gamma} \cdot \eta \cdot \dot{\gamma}$$

$$\text{with } \tau = \eta \cdot \dot{\gamma}$$

$$N = V_s \cdot \eta \cdot \frac{\dot{\gamma}^2}{\delta^2} \left[\frac{N \cdot m}{s} \right] \quad [69]$$

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This energy will cause a temperature increase ΔT of the sample volume V_s within time t

$$N = c \cdot \rho \cdot V_s \cdot \frac{\Delta T}{t}$$

$$\rho = \text{density of the sample} \left[\frac{\text{kg}}{\text{m}^3} \right]$$

$$c = \text{mean specific heat of the sample} \left[\frac{\text{J}}{\text{kg} \cdot \text{K}} \right]$$

K = temperature [K]

Rearranging gives the temperature increase for the time unit:

$$\frac{\Delta T}{t} = \frac{N}{c \cdot \rho \cdot V_s} = \frac{\eta}{c \cdot \rho} \cdot \dot{\gamma}^2 \quad [70]$$

This equation indicates that the temperature rise is proportional to the square of the shear rate and inversely proportional to the square of the ratio of the radii.

If tests at a high shear rate are required this usually leads to small gap sizes, i.e. the ratio δ is approaching 1.00. The resulting shear heating can be dramatic when tests are run for an extended period of time.

One does not have adiabatic conditions in real tests because heat is rapidly lost to the surrounding cup and rotor, but in samples with a low coefficient of heat conductivity heat is created faster during a high shear test than it can be lost to the outside.

Not even the most sophisticated modes of temperature control conceivable can prevent in such a case undesired temperature rises as the result of shear heating. This problem is less serious in capillary rheometers because they extrude most of this heat with the extrudate leaving the capillary.

In rotational rheometers high shear testing can cause the flow curve to deviate from its true pattern when critical shear rates are exceeded (see Fig. 106). This will be due to an accumulation of shear heat in the sample tested and the resulting viscosity drop. To minimize the effect of shear heating, it is good practice to plot flow curves not continuously but with intervals at rotor stand-still to allow periods of temperature recovery before further increasing the rotor speed stepwise from one speed level to the next higher.

Whenever measuring high viscosity samples at high shear rates, one should be aware of shear heating and its effects on the measured viscosity data.

8. Testing Two Important Rheological Phenomena: Thixotropy and Yield Value

8.1 Measuring thixotropy

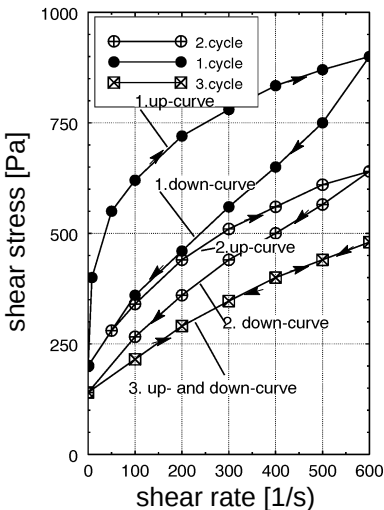
In the chapter “Thixotropy (pages 17–21)” the phenomenon of substances being shear-time dependent was introduced. Thixotropy describes a behavior of substances to change from a gel state of high viscosity to a much lower viscosity sol as the result of exerted high shear during some extended test period. An important criteria of thixotropy is the reversible process of re-thickening of the substance when left at rest. In principle the transformation from a gel to a sol and from a sol to a gel is endlessly reversible for real thixotropic substances.

Thixotropy is as such neither good nor bad, but for certain applications it can be favorable or negative. A paint that thins fast by strokes of a brush can be easily painted. When the applied paint layer on a vertical wall re-thickens fast this viscosity recovery will help prevent sagging. While an easy breakdown of thixotropic structures of a particular substance may be important to define a suitable motor for a mixer or blender and a low viscosity sol is favorable for the mixing with other ingredients, it is often the rate of structure recovery which carries the most important technical aspect of thixotropy: If re-thickening of a thixotropic dispersion is meant to prevent processes such as sedimentation and sagging, then it does not help if this fluid regains its gel state an hour or more after it was injected as a sol at high speed into bottles or containers. If such a fluid does not rebuild this gel structure almost instantaneously the settling ingredients such as particles of onions, paprikas, parsley etc. in salad dressing or the drug in the cough medicine will have dropped to the bottom of the container and they will never rise again on their own.

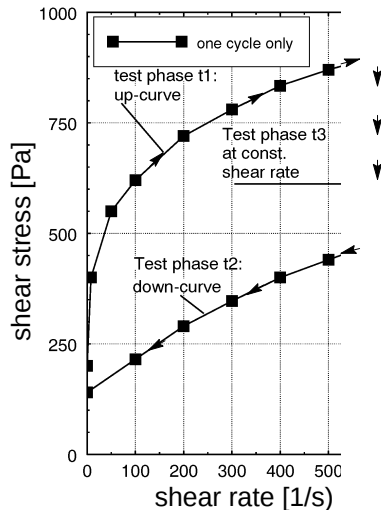
8.1.1 Measuring the breakdown of thixotropic structures.

a.) Determination of the magnitude of thixotropy of a fluid making use of a CR-rheometer and the evaluation of hysteresis curves.

This test procedure linearly ramps the shear rate within the periods t_1 and t_2 upwards and downwards and determines the resulting up- and down- shear stress curves – Fig 109. The up-curve positioned above the down-curve circumscribes an hysteresis area, which is proportional to the energy required to break down the thixotropic structure.



left: multiple up- + down ramps



right: single up- + down ramp

Fig. 116 CR-rheometer test of thixotropy: Determination of the hysteresis area between the up- and down-ramp flow curves

When the up-ramp is immediately followed by the down-ramp the total breakdown of the thixotropic structure may not have been achieved after a single up- and down cycle. A second, third or even fourth up- and down-cycle of such ramps with each time decreasing hysteresis areas may be required until the up- and down curves fall on top of each other to indicate that the sol status has been reached and all the thixotropic structure has indeed been destroyed by this extended shear – Fig.116, left side. It is in such a case common to program the test procedure in such a way, that the shear rate is maintained at its upper limit for a prolonged time t_3 , during which the structure breakdown is completed. When the shear rate is then programmed within the period t_2 back to zero, a wide hysteresis area is determined which in one single up- and down-cycle defines the magnitude of the thixotropy of the tested sample – Fig.116 – right side.

Modern computer software will calculate the integrals – the areas under the up- and the down-curve –, subtract one from the other and print the thixotropic energy in units of Joule/volume of the sheared sample.

Alternatively one can monitor with time the percentage of breakdown of a thixotropic structure for a given constant shear rate. The difference of the shear stress peak at the start of the test – gel level – and the asymptotically

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reached sol level of shear stress is an indication of the relative magnitude of thixotropy of a sample.

The tests as they have been described have one big drawback inasmuch as the test results are often difficult to reproduce for identical samples. Many dispersions have such feeble thixotropic structures that a sizable percentage of it is already partially destroyed just by introducing the sample into narrow and long shearing gaps especially of coaxial cylinder sensor systems. Since this filling is a human- dependent procedure this pre-shear can vary from one test to the next. It may take many minutes or even hours until the sample left at rest inside of the sensor system will have recovered its full gel state.

It is preferable for these tests of the total thixotropy energy to use cone-and-plate- or parallel-plate sensor systems and program a slow axial travel speed, being identical each time, to bring the cone or the upper plate to the assigned gap size with respect to the lower plate. Scooping a tea spoon of sample out of a container and placing it on the lower plate means little pre-shear. The final step of filling the shearing gap and squeezing some of the sample radially represents a more significant pre-shear, but it is maintained with the automatic and slow gap setting within a programmed, reproducible procedure in which human factors have been removed.

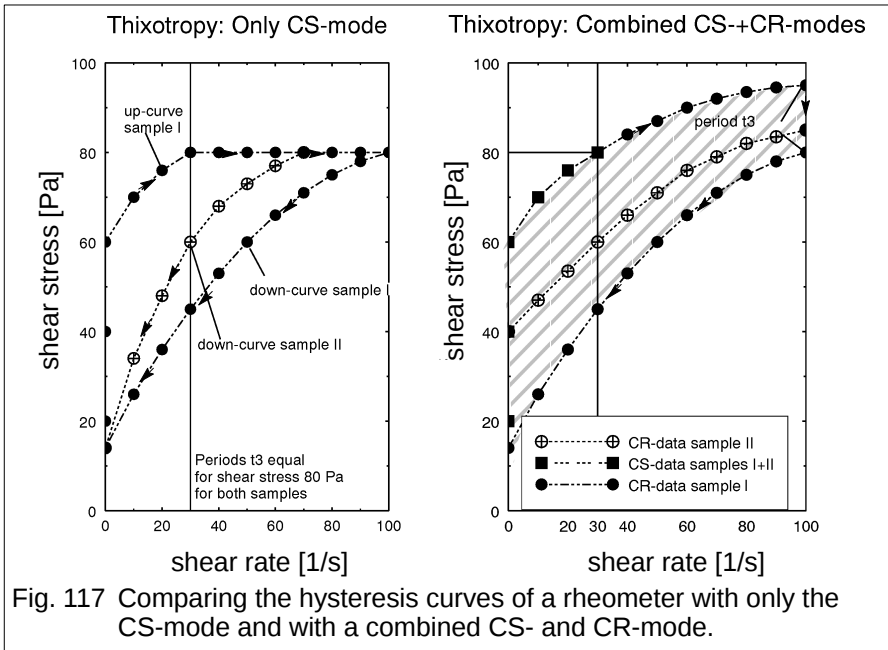
b.) Determination of the hysteresis curves by means of modern CS-rheometers with alternative modes of CS and CR.

It has been pointed out that in most test cases CS- and CR-rheometers provide identical results. But with respect to the evaluation of hysteresis curves there are differences between these rheometer modes worth pointing out:

It was explained that in a CR-rheometer a shear rate range was assigned and the upper shear rate value could be maintained for any time period t_3 until the thixotropic structure was fully destroyed. In a CS-rheometer one can assign a shear stress range, but one cannot maintain a constant resultant value of shear rate for any defined shear stress value independent of a given sample: If such a value is kept constant for some time t_3 the shear rate will continue to increase as the result of the thixotropic breakdown, i.e. the rotor will accelerate without limits set by the test program. When at the end of the period t_3 the shear stress is ramped down again the down-curve will start for different thixotropic samples at different values of shear rate, making a comparison of samples difficult – Fig. 116, left side.

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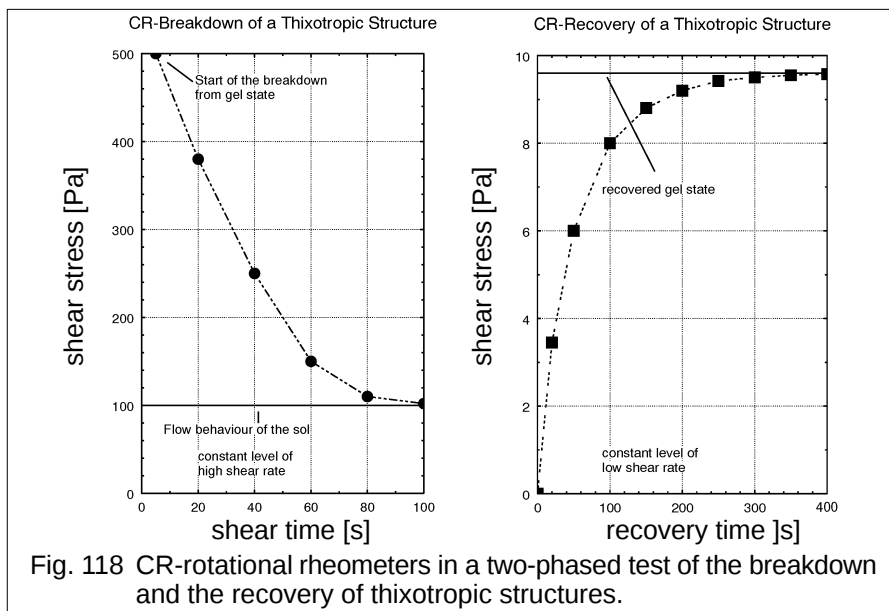
Making use of a rheometer set to its CS-mode provides – as will be explained later – well defined values of a yield value, which is almost always a second criteria of thixotropic fluids. In this respect the CS-rheometer-mode is superior to a CR-mode (see also Fig. 25), while this classification is reversed for the comparison of thixotropic structures. It therefore makes sense to program the rheometer for a combination of both the CS- and the CR-modes – Fig. 117, right side:

During the initial test phase in the CS-mode a ramped program for a shear stress range is assigned exceeding the yield stress. Having reached a preset default stress value the rheometer is programmed to change into the CR-mode, i.e. instead of presetting the stress and measuring the resultant rate of deformation, now the shear rate is programmed to ramp upwards to its upper limit value and the resultant shear stress is measured. As it has been mentioned before one can keep the maximum shear rate constant (still in the CR-mode) for any assigned period t_3 and then ramp the shear rate down again to zero still in the CR-mode. While the up-curve is a combination of a CS- and a CR-segment the remainder of the hysteresis loop is taken only in the CR-mode. The combination of both modes provides the positive aspects of both: a precise yield value and a good comparison of the thixotropic energy of the samples I and II.

8.1.2 Measuring the rate of recovery of the gel structure of a sheared thixotropic fluid

a.) The CR-rheometer used in its CR-mode determines for assigned values of high and very low values of constant shear rates the shear stress/time-function during the breakdown and the recovery phase of thixotropic fluids.

Any good CR-viscometer and rheometer will show the thixotropy related shear stress/viscosity decay with time for given high levels of constant shear rates.



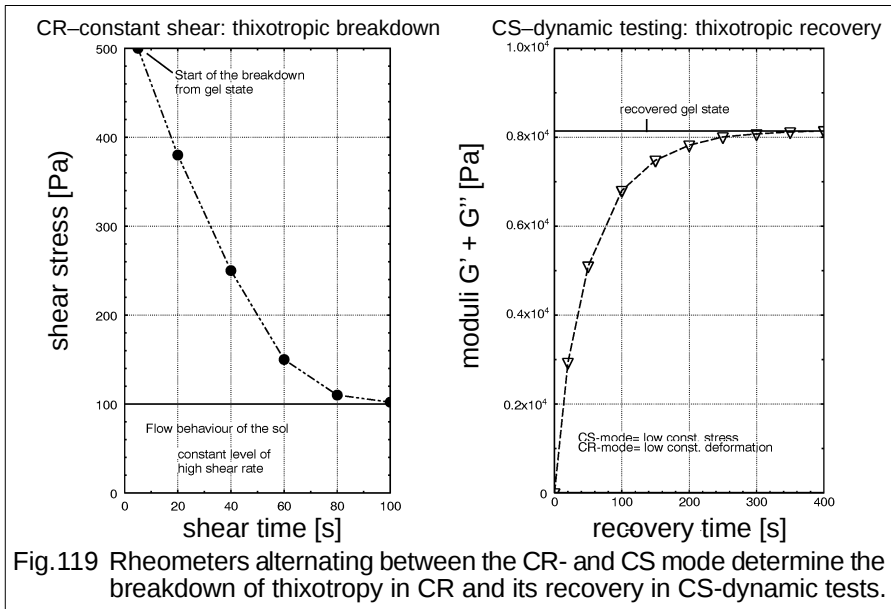
Measuring the rate of recovery is often of higher technical importance than the rate and amount of breakdown, because it is this rate of recovery which is an essential factor for settling, sagging and levelling. The recovery requires in principle that the fluid in its sol-state rebuilds its structure at rest. One cannot measure rheological responses to zero deformations and therefore one has to choose at least some small values of shear rate, which are sufficiently low to allow the recovery of intermolecular structures and which are not too high to break down any feeble structure that is just about to be rebuilt. Normal viscometers and rheometers run into problems, because they are not sensitive enough to measure significant stress data at very low values of shear rates. Rheometers with air-bearings for the rotor shaft and incremental deformation sensors such as the HAAKE RheoStress RS100 are designed for such a high sensitivity to determine meaningful recovery data. Fig. 118 indicates how the shear stress – or the viscosity which shows a similar pattern – increases with

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time, when the sample is subjected to a very small, time-constant level of shear rate simulating a “close to a stand-still-condition”. Recovery is in contrast to the breakdown of a thixotropic structure a longtime process which can require to full gel state many minutes, often hours and sometimes days. But even if one does not want to wait that long it is still important to discover whether the initial rate of recovery is high or low, i.e. what the percentage of recovery is in the first 5 to 10 minutes that would matter with respect to sagging, settling etc.

b.) The CS-rheometer is used in a first test phase in its CR-mode to breakdown thixotropic structures, but it is in a second phase shifted to its CS-mode and run in the dynamic test procedure to measure the rate of the recovery of thixotropic fluids – Fig. 119.



In comparison to the previous paragraph the method of the recovery is different only in the second test phase. Instead of assigning low, time-constant shear rates one can make use of dynamic testing: the sample is subjected to oscillating small deformations and as the result of a recovery of thixotropic structures one can measure the resultant increase of the storage modulus G' and/or the loss modulus G'' . The advantage of this method is that the molecules are indeed left at rest, i.e. the molecules that can form a gel network are not hindered by this particular test method: Before bonds between molecules or between volume elements of the dispersed phase are ruptured by the small stress acting in one direction, the direction is reversed.

8.2 The measurement of yield stresses

Rheologists have for years debated whether there is “something like a yield stress”. It has been stated that if one just waits long enough even “mountains can flow” or the glass panes in the cathedral of Chartres become thin at the top and thicker at the bottom. Even solid glass is in fact a Newtonian liquid of extremely high viscosity at a shear rate which for the flow of these glass panes has been estimated as $\dot{\gamma} < 10^{-10}$ 1/s. But everyone knows that glass can be considered a brittle, hard solid. It may be considered an “academic” question whether a yield stress can exist in real fluids. If practical experience indicates that something like it may be found and used beneficially in technical applications in a context of relevant time spans reaching from seconds to hours or days, then it should be used..

The idea of a yield stress – yield point, as it is often called – is that a limit stress exists below which a sample behaves as a solid: the stress deforms the sample elastically – as the spring model – and this deformation will totally disappear once the deforming stress is removed. Below the yield stress there is a linear proportionality between the assigned stress and the deformation. Volume elements are temporarily deformed but they are not changing their place irreversibly.

Above the yield stress the sample actually starts to flow: the assigned stress leads to an unlimited deformation and the stress is now related to the rate of deformation with the viscosity being the correlating factor.

Whether something may flow in some hundreds of years is irrelevant for anyone who produces, i.e. a bread-spread or marmelade. Once applied to a slice of bread it must not flow off within the next 2 to 3 minutes before a child will eat that slice. We expect that a bit of tooth paste forced out of its tube onto the bristles of the brush will stay there in its cylindrical shape until we start brushing our teeth and we know by experience that some paint does not sag off vertical walls or particles in some dispersions are prevented from settling. Obviously some samples allow the formation of intermolecular and/or interfacial bonds within dispersions which result in temporary networks and which resist destruction by shearing forces below a critical stress level. This stress can be measured and it is common to use the term “yield value” for it.

8.2.1 Making use of a CS-rheometer for the measurement of yield stresses.

The measurement of yield stresses is the ideal domain of controlled stress rheometers. They allow one to program stresses to increase until the assigned stress surpasses the yield value and the sample starts to flow. The stress applied acts directly on the rotor which in coaxial cylinder sensor systems is surrounded by the sample which below the yield value can be considered a

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solid bonding of both outer cylinder and rotor. Only when the applied stress surpasses this yield value characterizing the sample in the annular gap can the rotor start to turn at a meaningful shear rate. When plotting a CS-flow curve with the assigned stress on the ordinate and the resulting shear rate on the abscissa – more common than the reversed assignment to the coordinates – the data points rise vertically on the ordinate until at the yield stress the flow curve breaks away from the ordinate: this has already been shown in Fig. 25. The point of deviation of the flow curve from the initial vertical rise on the ordinate is normally quite distinct and it therefore allows one to pinpoint this critical stress clearly. This diagram also indicates the difference in both the yield values as measured by a CS- and CR-rheometer. Fig.120 shows the flow curves of 2 ketchup samples, which shows the differences with respect to their yield values and their thixotropy. The tests were run with a combination of the initial CS-mode which was followed by the CR-mode for the continuation of the flow curve. To determine the yield values of these samples even better one can choose to plot the diagram with a very much reduced shear rate ordinate as shown in Fig.121.

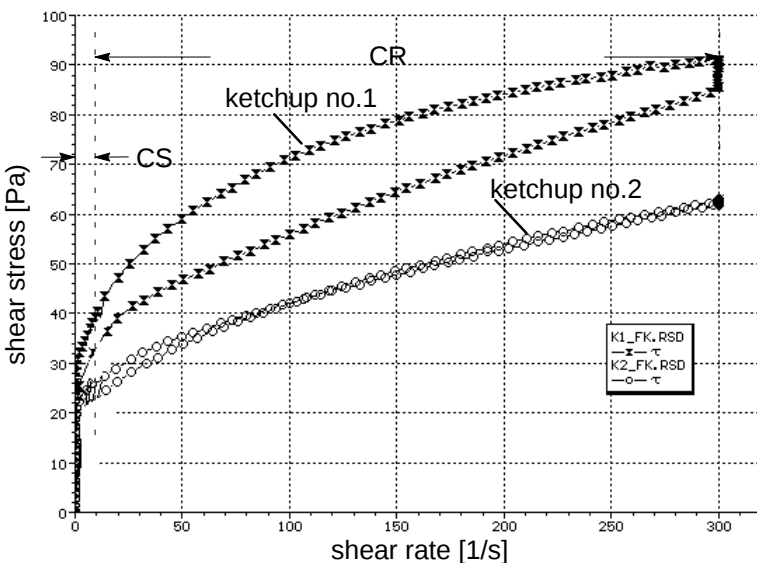


Fig. 120 A CS-rheometer used for the up- and down-ramps of flow curves of two ketchup samples differing both in their yield values – marked in the CS-mode – and their thixotropic flow behavior determined in the CR-mode

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8.2.2 Making use of a CR-rheometer for the determination of yield stresses.

Fig. 25 presented the yield point measurement with a CR-rheometer equipped with spring-type torque sensor. This sensor used a “soft” spring which required a 90° deflection for the measurement of the full torque range. Such a rheometer was designed with a directly linked motor/tachometer. The speed signal is not provided by the rotor but from the tachometer which is linked only by the flexible torque spring – 90° angle of twist for the full torque range. Below the yield stress motor and rotor speed are different: the motor already is programmed to start rotation while the rotor is clamped at stand-still by the surrounding sample. The tachometer-generator produces a speed signal and the resulting deflection of the torque spring provides a τ -signal which is linearly related to the spring coefficient of the sensor but is not characteristic of the sample. The flow curve as determined by a CR-rheometers/viscometer below the yield value starts from the origin with a linear upwards sloping curve segment with an angle that does clearly deviate from the vertical. At the yield value the rotor breaks loose from the sample in the annular gap, the rotor speed accelerates almost momentarily to the motor speed at that moment. When the shear rate ramp program is further continued both motor and rotor speeds remain identical. The flow curve changes quite apparently its slope when the yield stress is surpassed. It is a common procedure to define the corresponding ordinate value of this turning point of the flow curve as the yield stress even if this value is often a bit higher than the yield value as measured by a CS-rheometer.

More recent CR-rheometers designs use a “rigid” spring or torsion element which for a 0 to 100% torque range only deflects 0.5° . Yield value measurements are then best performed in the “controlled deformation mode” (CD) with a test of torque versus time at a constant low rotor speed. For samples showing a yield value the torque rises first to a peak. Since most samples with a gel structure are highly thixotropic the torque curve drops normally quite rapidly once the peak has been surpassed. The peak characterizes the yield value of the sample. The torque curve leading to the peak is slightly inclined with respect to the ordinate indicating that the rotor just slightly moved. This can be interpreted as an indication of some creep and perhaps of some elastic deformation of the sample in the gap between rotor and cup before the real flow starts once the yield value of the sample has been surpassed.

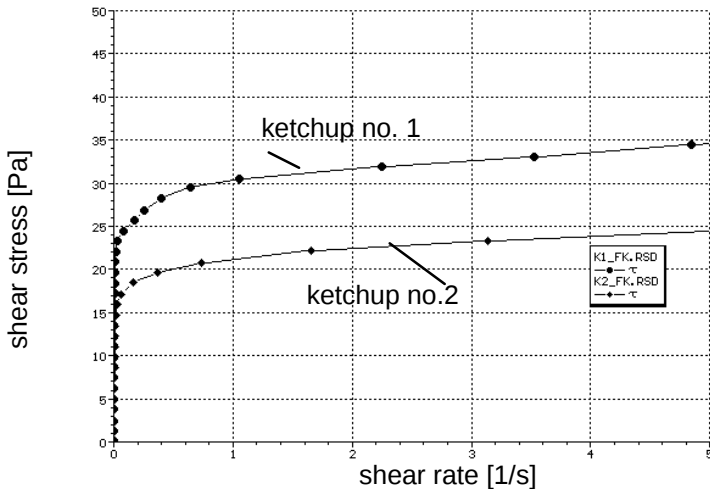


Fig. 121 Expanded segment of the initial flow curve of Fig. 120

8.2.3 The importance of τ_{01} and τ_{02}

A comparison of Fig. 120 and Fig. 121 indicates that flow curves even of a CS-rheometer covering a wide shear rate range are not ideal to pin-point the yield stress. It is worthwhile to expand the shear rate data in a very much reduced range – here between $\dot{\gamma} = 0$ to 5 1/s – to determine the yield values of the K1 and K2 samples as $\tau_1 = 24$ Pa and $\tau_2 = 16$ Pa. The non-exact values taken from Fig. 120 would have been $\tau_1 = 30$ Pa and $\tau_2 = 22$ Pa.

The determination of accurate yield values requires test conditions with a suitable torque range: the yield value is at least 40 or more percent of the torque range and consequently the percentage of error of the yield value is kept small. If a preliminary test showed a yield value being only less than 10 % of the chosen torque range, then one should select other sensor systems with rotors of larger surface area – smaller torque factors A – producing under otherwise identical test conditions higher values of yield torque. This is especially important for the measurement of the yield value of the down-curve during the τ_3 period: This retained yield value which in dispersions is able to act momentarily against settling and sagging of a sample that had been transformed in previous production steps to a sol of a low viscosity. Even the most rapid thixotropic recovery of a network structure may be too slow if the particles sediment during the first few moments at rest. Literature often differentiates between the up-curve yield value τ_{01} and the down-curve τ_{02} . The latter is in most cases technically more important than the τ_{01} . The great majority all viscometers/rheometers in world-wide

use are of CR-design and they are almost always insufficiently accurate for the measurement of τ_{02} -values. τ_{02} -values are rarely mentioned in technical literature and in many laboratories their importance with respect to product quality criteria such as shelf life of stored products is underestimated. It is hoped that with the new generation of modern, much more sensitive CS-rheometers this situation will change.

Many viscometers of lower price do not provide continuous flow curves but a pointed flow curve. It is common to extrapolate such a flow curve beyond the lowest shear rate data towards the ordinate in order to get some indication of the τ_{01} and τ_{02} . If one had done this in Fig. 120 for the down-curve K1 assuming that the lowest fixed shear rate provided in the viscometer was $\dot{\gamma} = 25 \text{ 1/s}$, then the extrapolated down-curve would hit the ordinate at $\tau = 35 \text{ Pa}$, which is about double the true τ_{02} . Near the yield value the flow curves are highly bent!

8.2.4 Making use of double logarithmic scaling for flow curves of thixotropic dispersions to extrapolate to the yield value.

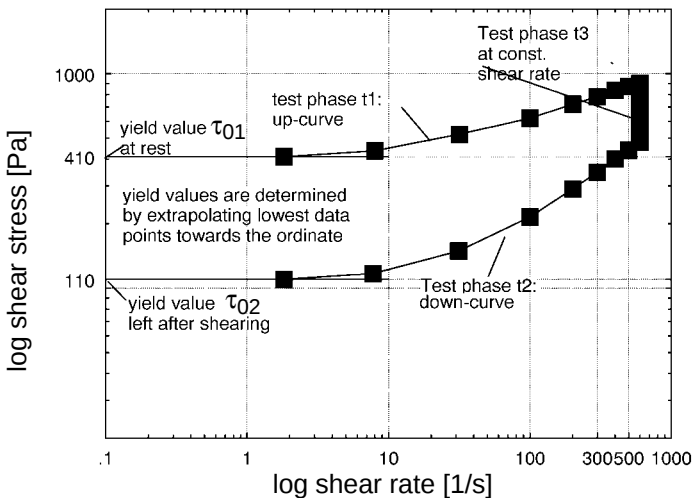


Fig. 122 CR-rheometer flow curve of a dispersion characterized by its yield values and its thixotropy plotted in double logarithmic scaling for the extrapolation to the ordinate to define yield values.

For a comparative differentiation of thixotropic fluids it is sometimes worthwhile to look into the potential of another method of extrapolation: If one plots hysteresis curves of thixotropic samples with double logarithmic scaling, one will often find curves as in Fig. 122. If there are sufficient data in the low shear

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rate range, especially for the down-curve, they will level horizontally. Extrapolating towards the ordinate then provides quite a reasonable yield value.

8.2.5 Plotting deformation versus assigned shear stresses.

The new CS-rheometers offer a new method to determine yield values. They allow ramping the shear stress τ and measuring the resulting deformation γ – Fig.123. The sensitivity of the incremental strain sensors starting from a deformation of $\gamma = 0.01\%$ or less provides significant data already for very small stresses. The measured results will show two curve segments. The first segment is a line with a slope of one: the sample is elastically deformed and the slope of τ versus γ represents the “spring coefficient” of the fluid below its yield value. At the yield value the curve turns into its second segment: the slope angle changes much indicating the start of volume flow.

In order to digitally define such a yield value the software allows one to determine by means of regression the slopes of each segment and a determination of the cross-over point.

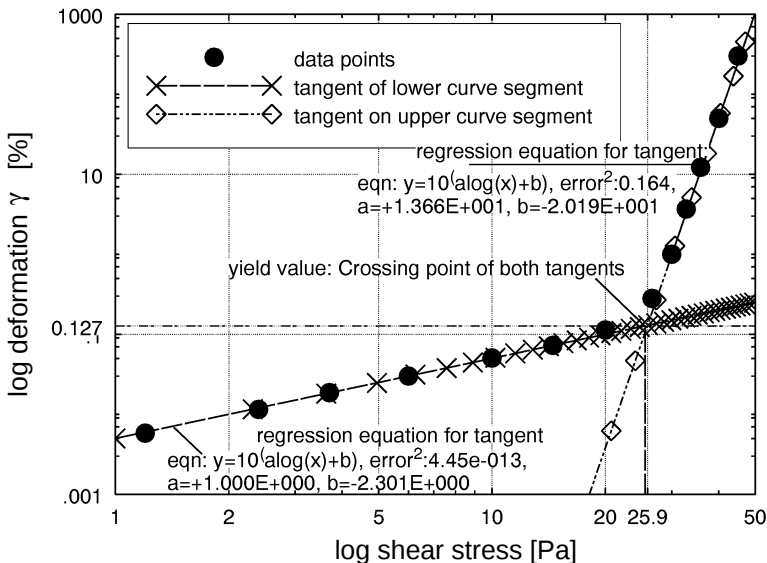
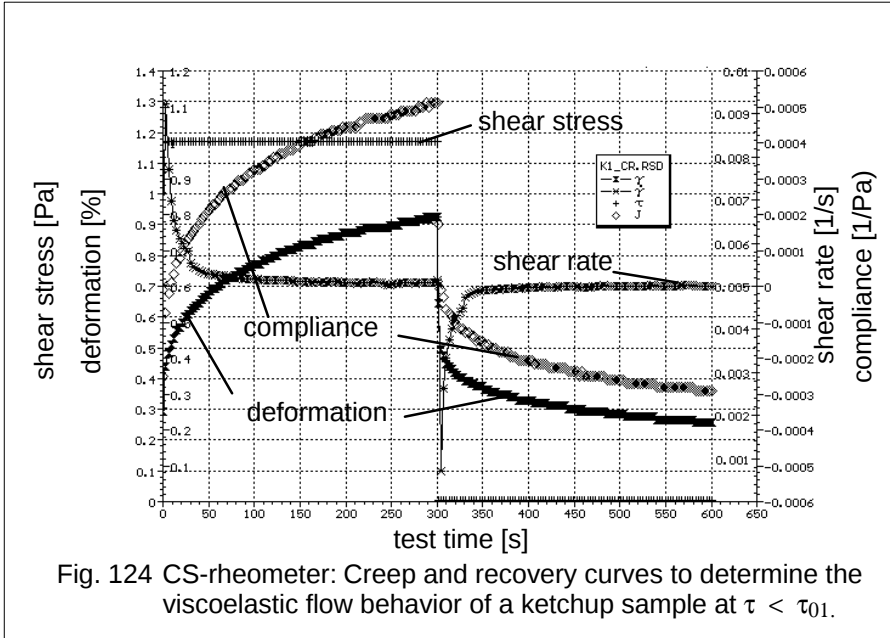


Fig. 123 CS-rheometers to determine yield values in a diagram of shear stress versus deformation

8.2.6 Creep and recovery curves to determine a sample's below-the-yield behavior



Dispersions are visco-elastic and it is worthwhile to check whether the creep and recovery test can also provide yield related information. Fig 124 is the result of tests with a Ketchup sample K1. This time the deformation γ and the shear rate $\dot{\gamma}$ is determined with respect to time with a constant shear stress $\tau = 1 \text{ Pa}$ as the input. Creep tests indicate that such a sample will elastically deform at increasing small stress values until the deformation curve breaks away from the ordinate and that then a simultaneous viscous and elastic response occurs during the further deformation phase.

In the recovery phase one can differentiate between the two responses. One follows the retardation curve to determine how much of the previous deformation can be elastically recovered if "infinite" time is available. Once the retardation curve has levelled horizontally the retained deformation marks the amount of viscous flow while the amount of recovery is a measure of elasticity.

Inasmuch as different stress levels – within the limits given by the linear-visco-elasticity – show families of creep and recovery curves, it makes sense to transform the creep curves to the corresponding compliance curves J , which "eliminate" the stress parameter.

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These creep and recovery curves indicate that “much” happens before the sample really starts to flow, but it is this response that can be used to link rheological behavior to a sample’s composition and homogeneity. The yield value is an important rheological value but one must always keep in mind that it is also a transient value and that it cannot be considered as a “constant” completely characterizing a solid’s behavior once and for all. Fig. 25 compares two ketchup samples indicating their difference in yield and rates of recovery.

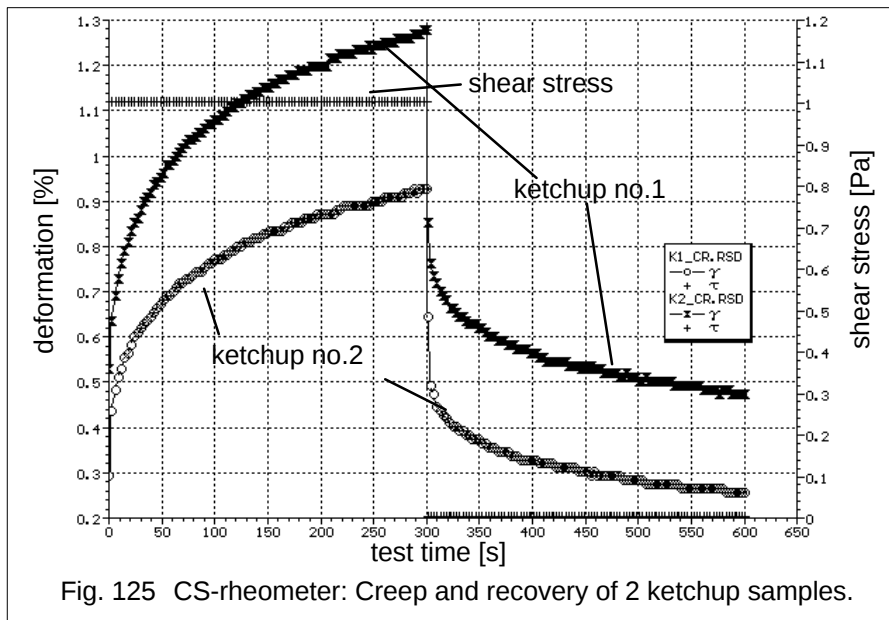


Fig. 125 CS-rheometer: Creep and recovery of 2 ketchup samples.

8.2.7 The use of vane rotors for the measurement of yield values.

Making use of vane rotors – star-shaped rotors – provides a test method which looks on first sight quite primitive, but it is in fact often the best method for the testing of dispersions with a very weak thixotropic structure. It has been mentioned that placing such a thixotropic sample into the annular gap of coaxial cylinders or in the gap of a cone-and-plate often partially destroys the thixotropic structure. Waiting for a complete recovery of this structure can be minutes or hours and for yoghurts this recovery never occurs since its biological structure cannot be rebuilt once it has been mechanically broken by shear.

It is the great advantage of vane rotors that they may be submerged into samples which may be left undisturbed in their commercial beakers as used for yoghurts, ice-creams, desert jellies etc. In factories of these products one can place 10 or 20 of these beakers into a refrigerator overnight, so that next

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morning the samples all have the right and equal temperatures. The samples are tested in their beakers, i.e. there is no need to fill them into the normal sensor systems of the rotational viscometers/rheometers. The beakers are just positioned underneath the vane rotors in a proper fixture. In a CS-rheometer such as the RheoStress RS100 the lower fixture is programmed to move upwards until the vane rotor is axially sunk into the sample. The thin rotor blades just cut knife-wise into the sample but do not disturb the thixotropic structure of the mass situated in the space between the vanes nor the mass outside the reach of the rotor. When torque is applied to the rotor a shearing stress acts on the surface of the cylinder formed by the rotor.

when the rotor breaks loose inside of the sample having passed its yield value it forms a rotating cylinder of the diameter "a" and the height "h".

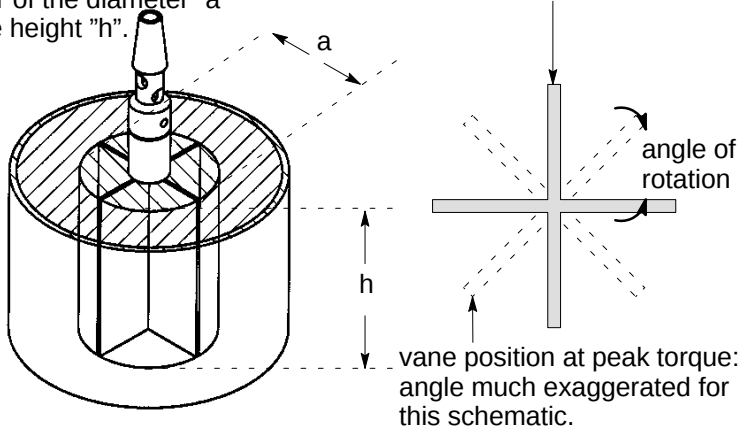


Fig. 126 Vane rotors in a large container filled with samples are used to rapidly determine the yield point of samples such as yoghurt

When the yield value of the sample is surpassed the cylinder formed by the vane rotor breaks loose within the sample. The rotor – so to speak – drills a hole into the sample. In samples such as yoghurt the outside mass stays stagnant just as the mass inside of the rotor cylinder. Only the mass in the very thin boundary layer between the rotating cylinder and the outside mass is highly sheared, its thixotropic structure is momentarily broken completely and the resistance of the sample against being sheared in that boundary region drops sometimes almost to zero in seconds or less. This is a very simple and rapid test: having used a refrigerator overnight, one does not need extra time for proper temperature control. Removing the beakers from their temperature controlled storage room and testing the samples a minute later means that the

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test temperature is equal to the storage temperature. Having placed the vane rotor into the sample a stress-ramp program is started. One determines at what stress level the rotor starts to move. When testing samples such as yoghurt the test is finished within a fraction of a minute. Once the yield stress of the sample is surpassed and the rotor breaks loose inside of the stagnant outer mass the stress applied will accelerate the rotor momentarily to its maximum speed. The flow curve – Fig.127, squared data points – indicates clearly the instantaneous change of response pattern to the applied shear stress. Additionally the deformation – Fig.127, round dots – indicates that up to the yield point the sample is highly deformed until the vane rotor drills a cylindrical hole into the mass. At the yield point the deformation exceeds a preset limit and it is no longer measured nor data points are plotted. The deformation curve indicates that “much” happens long before the sample yields in the boundary layer between the cylinder which is formed by the contour of the vane rotor and the mass further outwards.

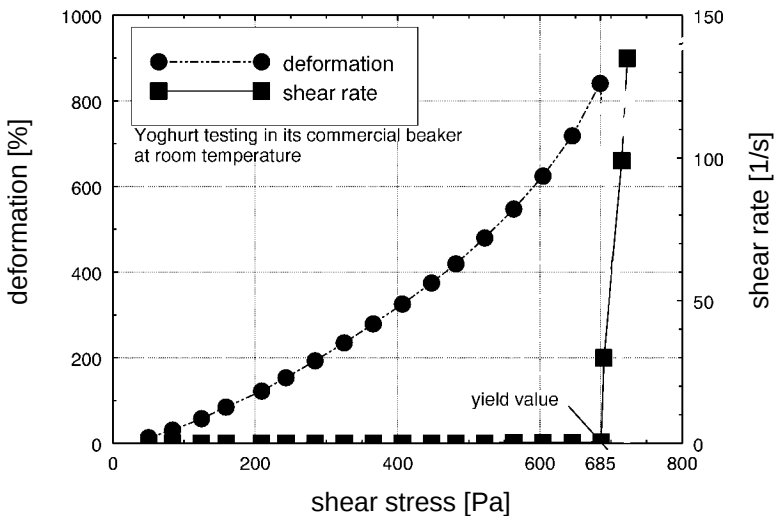


Fig. 127 CS-rheometer used in a creep tests to determine yield values

This type of yield value test takes a minute or so. It should be possible to determine the yield values of 10 samples in some 20 minutes. It is an indication of the “strength or firmness” of samples related to their composition, homogeneity, state of gelling, ability to stand-up to transport vibrations and the safety against a phase separation during long-term storage. While the yield

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value is mathematically well defined in vane-tests, the interpretation of this measured value has a relative character for any product and its quality.

This type of test does not require a sophisticated CS-rheometer. Simpler CR-viscometers providing a range of fixed rotor speeds/shear rates with a recorder outlet may be run at a low speed level. The resulting shear stress is plotted versus test time. The curve rises to a peak and then drops again. The peak torque defines the yield value of the sample. Normally the test is terminated shortly after passing the peak – Fig. 128.

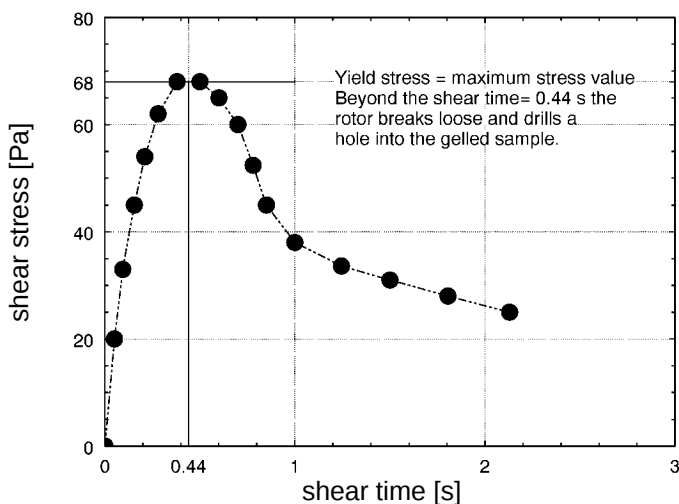


Fig. 128 CR-rheometer: Yield point measurements with a vane-type rotor

This latter part of the curve beyond the peak – the slope of this curve segment and the level it reaches asymptotically – is most of time outside the scope of interpretation, because it cannot be defined how wide the sheared boundary layer around the rotor cylinder is, e.g. how much of the sample in its beaker is actually reacting to the applied stress.

This vane rotor method works well to determine the static yield value of a gel. The rotor is not able to shear thin all the mass in its beaker so that the sol-state cannot be reached. It therefore does not make sense to try to measure a meaningful τ_{02} -value in an hysteresis down-curve.

Assuming that the sample yields along the cylindrical and both the upper and lower disk-type end-face surfaces – disregarding the small diameter rotor shaft – one can use the following equations:

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Torque M_{d-e} acting on both end faces of the vane rotor:

$$M_{d-e} = 2 \int_0^r 2 \cdot \pi \cdot r^2 \cdot \tau_0 \cdot dr = 4/3 \cdot \pi \cdot r^3 \cdot \tau_0$$

Torque M_{d-c} acting on the cylindrical vane surface:

$$M_{d-c} = 2 \cdot \pi \cdot r^2 \cdot h \cdot \tau_0$$

Total torque M_d acting on a vane rotor:

$$M_d = M_{d-c} + M_{d-e} = (2 \cdot \pi \cdot r^2 \cdot h + 4/3 \cdot \pi \cdot r^3) \cdot \tau_0 = 2\pi \cdot r^2 \cdot \tau_0 (h + 2/3 \cdot r) \quad [66]$$

M_d = measured torque,

τ_0 = yield stress

h = height of rotor,

r = radius of the vane rotor

a = diameter of vane rotor → see schematic Fig.126

The larger the ratio of $h : a$ is, the smaller is the contribution of the end faces on the measured yield stress τ_0 . This may be checked by running tests using a family of vane rotors which differ in height but not in their diameter. To keep wall effects small the diameter of the test vessel/beaker should be at least twice the rotor diameter and the rotor should be submerged into the vessel so that the distances from the rotor to the bottom of the beaker and to the sample's upper surface equal the size of the rotor diameter.

Please note: Testing thixotropic samples reproducibly – the total energy to break down its structure, the rate of recovery and the size of its yield value – is difficult, because the handling of the sample prior to the actual test is so influential on the test data. One must design a suitable test procedure and **stick to it** in order to reduce any operator influences. The vane rotor method helps with respect to the yield point determination and it requires just medium price range viscometers provided with a recorder outlet.

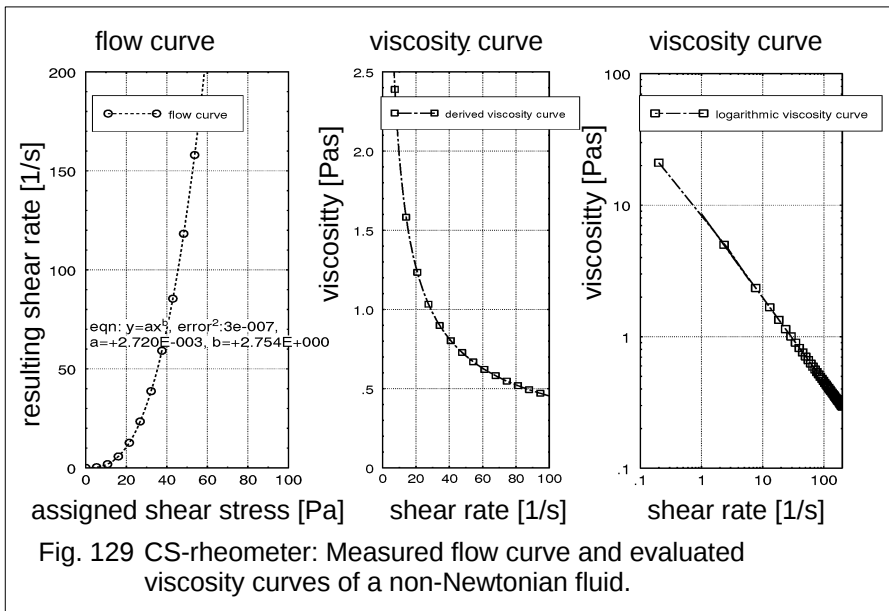
9. Mathematical Treatment of Test Results for Non-Newtonian Liquids

9.1 Transformation of flow to viscosity curves

Good sensor systems for rotational rheometers allow the mathematical treatment of shear stress and shear rate in steady state flow and in dynamic testing. The relationship between the two – now-a-days usually plotted automatically as a flow curve – describes the flow behavior of any sample. The flow curve could be termed the rheological “finger print” of a sample. Several different samples are best compared by a comparison of their flow- and viscosity curves covering as wide a shear rate range as possible or as required for their processing.

 **Please note:**

Rheological testing always first provides the correlation between the assigned shear stress and the resulting shear rate (CS-rheometers) or between the assigned shear rate and the resulting shear stress (CR-rheometers).



The **flow curve** which has been measured and plotted is for many people of limited use. They rather want **viscosity curves** which seem to be more meaningful as they define how non-Newtonian liquids shear-thin with increasing shear rates or increased pumping rates for flow through i.e. pipe lines.

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It is the great advantage of modern computers to provide this transformation of flow to viscosity curves within seconds and without the "hard labour" of a manual recalculation of the data. This transformation does not provide "better" but more meaningful data for quite a number of people.

The same is true for viscosity curves in double logarithmic scaling which in comparison to viscosity curves in linear scaling gives a better insight into the rapid viscosity change of e.g. whole blood at low shear rates.

9.2 Considerations with respect to the evaluation of relative and absolute viscosity data

Condensing the flow curve of a Newtonian liquid to a single digital value characterizing such a sample rheologically is simple and sufficient: The straight line flow curve, which is the result of a test of a Newtonian liquid in a rotational rheometer and a cone and plate sensor system – dashed line in Fig.130 –, has a constant slope α_1 and a constant $\tan \alpha_1 = \eta$. Viscosity of such a liquid is independent of shear rate.

$$\tau = \tan \alpha_1 \cdot \dot{\gamma} = \eta \cdot \dot{\gamma}$$

Testing non-Newtonian liquids and deviding the corresponding pairs of shear stresses and shear rates for several points on the non-linear flow-curve – the continuous line in Fig. 130 – will give changing values of viscosity which are meaningless unless they are always backed by the corresponding values of shear rate:

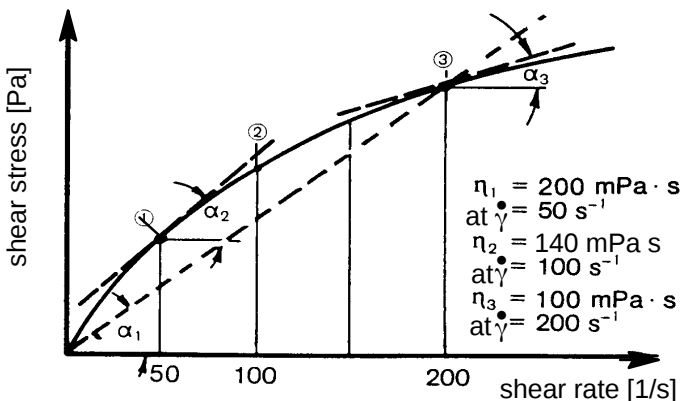


Fig. 130 CR-rheometer with a cone/plate sensor system used for the comparison of the flow curves of a non-Newtonian– and a Newtonian liquid at $\dot{\gamma}_3$ and other shear rates.

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Fig. 130 shows the flow curve of a non-Newtonian fluid – the continuous line. At three points of this curve viscosity values $\eta = 200, 140$ and $100 \text{ mPa}\cdot\text{s}$ have been calculated for shear rates of $\dot{\gamma} = 50, 100$ and 200 1/s . At point ③ this non-Newtonian fluid has, at the shear rate of $\dot{\gamma} = 200 \text{ 1/s}$, an identical viscosity η_3 as a Newtonian liquid with a straight flow curve – dotted line in Fig. 130 – with the slope of α_1 passing through both ③ and the origin of the diagram.

While the value η_3 is alike for both the Newtonian and the non-Newtonian liquids it does not mean that their flow behavior is really the same: at higher and lower shear rates the viscosity of the Newtonian liquid remains the same but the viscosity values of the non-Newtonian liquid change dramatically and so do the tangents on the flow curve left and right of point ③.

Working with CR-rotational viscometers and rheologically correct sensor systems such as "cone & plate" providing a single or a limited number of fixed rotor speeds will allow the evaluation of absolute viscosity data. These represent one or a few points on a segment of the viscosity curve covering only a very limited shear rate range. Especially when for a particular non-Newtonian fluid the production process or its application and therefore the relevant shear rates are not known, the absolute viscosity data have a relative character for the classification of different samples or batches: "lower" or "higher" viscous. Today most viscometers and rheometers plot flow curves continuously, which are automatically transformed to viscosity curves. This allows a better but still more or less relative comparison of samples on the basis of the continuous viscosity curves covering wide shear rate ranges.

A relative comparison is not sufficient if rheological data of non-Newtonian fluids must be directly compared, which have been determined by means of different types of "absolute" viscometers and rheometers. Deviations between results on identical samples may be caused by the characteristics of the particular non-Newtonian fluid and its deviation from the true Newtonian behavior and on technical difficulties to avoid more or less significant "errors" i.e. in the measurement in relevant pressure drops or shear stresses in capillary viscometry. Working with equations relevant for Newtonian liquids for the evaluation of viscosity data of non-Newtonian fluids and neglecting the "errors" will lead to – what is called – "**apparent**" viscosity data, which most of the time will be considered sufficient for distinguishing different samples with respect to their practical usage. They have to be converted to "**true**" viscosity if data gained by different instruments require a direct comparison:

1.) The shear rate in cone/plate-sensor systems is well defined being constant from the cone center to its outer radius. This is not the case for plate/plate-sensor systems, which provide shear rates changing from zero at the center to the maximum at the rim of the rotating plate. Calculating the maximum shear rate and calling it relevant for the whole gap between the plates as the basis

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for the evaluation of the viscosity of a non-Newtonian liquid provides only a relative **apparent** viscosity signal, which allows the relative rheological classification of different samples. These data cannot be directly be compared to those of i.e. cone/plate-measurements linked to correct values of shear rate. Only by means of "corrections" can plate/plate-data be transformed into **true** viscosity data as those provided by the cone/plate-sensor system (Fig. 140).

2.) In capillary viscometry Newtonian liquids will show a parabolic flow profile across the capillary and a linear shear rate- and shear stress decrease from the capillary wall to its center. When testing non-Newtonian, viscoelastic fluids the flow profile across the capillary changes to a flattened parabolic shape and a shear rate profile, that is no longer linear starting from a much higher maximum at the capillary wall and decreasing faster when approaching the center – Fig. 87: center of schematic.. In rod die viscometrie – Fig. 135 – it is in addition difficult to determine that pressure drop ΔP required to calculate the correct shear stress value. Taking as this pressure drop the pressure difference measured by a pressure sensor placed at the entrance of the capillary and the ambient pressure at the exit of the capillary will introduce a grave error when calculating the relevant shear stress. This pressure difference incorporates also entrance- and exit effects and it therefore does not represent just the pressure to overcome the resistance of the fluid when forced to flow through the capillary. Without "corrections" – chapter 9.5 – both on the shear stress and on the shear rate values the evaluated viscosity data are **apparent**. Making use of the Bagley- and the Weissenberg/Rabinowitsch-corrections they can be converted to **true** viscosity data.

When flow and viscosity curves plotted in double logarithmic scaling give straight lines, it is an indication that the Ostwald-de-Waele equation can be safely used.

$$\tau = K \cdot \dot{\gamma}^n \rightarrow \tau = \eta \cdot \dot{\gamma}$$

Please note: for $n = 1 \Rightarrow$ "K" converts to " η ", thus describing Newtonian flow behavior. The more "n" deviates from "1" the more shear rate dependent the fluid viscosity becomes.

Example:

Increasing the pressure ΔP four-fold to extrude an Newtonian fluid will quadruple the flow rate Q in a pipe line [26]: $\dot{\gamma} = (Q/c_2) \Rightarrow 4 \dot{\gamma} = 4 \cdot (Q/c_2)$

Increasing the pressure or shear rate similarly four-fold for a non-Newtonian melt with a relatively normal exponent of $n = 1/2$ will cause a 16-fold increase in the flow rate Q .

$$Q = c_2 \cdot \dot{\gamma}^n \Rightarrow \dot{\gamma} = (Q/c_2)^{1/n} \Rightarrow n = 1/2 \Rightarrow \dot{\gamma} = (Q/c_2)^2 \Rightarrow 4 \dot{\gamma} = 16 \cdot (Q/c_2)^2$$

c_2 = constant related to the geometry of the pipe line.

This example again draws the attention to the fact that the non-Newtonian behavior of fluids can have quite an important technical relevance.

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9.3 Curve-fitting with rheological equations

It is a normal procedure in rheology to use regression calculations for curve-fitting on plotted flow and viscosity curves. Seventeen different mathematical equations with rheological significance (Fig. 131) and further polynomial functions are provided by the HAAKE software, which can be used for this curve-fitting. The computer is programmed to find the best-fit coefficients for a chosen equation and to print "the level of uncertainty" describing the statistical relevance of the fitted curve to the measured test points.

flowcurve - models ($\tau=f(\dot{\gamma})$)	
Newton	$\tau=\eta\dot{\gamma}$
Bingham	$\tau=\eta_p\dot{\gamma}+\tau_0$
Ostwald-de-Waele	$\tau=K\dot{\gamma}^n$
Herschel-Bulkley	$\tau=K\dot{\gamma}^n+\tau_0$
Casson	$\tau=\sqrt{\tau_0^2+(\eta_p\dot{\gamma})^2}$
Cross	$\tau=\dot{\gamma}(\eta_{\infty}+(\eta_0-\eta_{\infty})/(1+(\dot{\gamma}/\dot{\gamma}_b)^n))$
Carreau	$\tau=\dot{\gamma}(\eta_{\infty}+(\eta_0-\eta_{\infty})/(1+(\dot{\gamma}/\dot{\gamma}_b)^2)^n/2)$
Meter	$\dot{\gamma}=\tau/(\eta_{\infty}+(\eta_0-\eta_{\infty})/(1+(\tau/\tau_0)^n))$
Tscheuschner	$\tau=\dot{\gamma}(\eta_{\infty}+\tau_0/\dot{\gamma}+\eta_p/(\dot{\gamma}/\dot{\gamma}_b)^n)$
Viscosity - models ($\eta=f(\dot{\gamma})$)	
Newton	$\eta=\text{constant}$
Bingham	$\eta=\tau_0/\dot{\gamma}+\eta_p$
Ostwald-de-Waele	$\eta=K\dot{\gamma}^{n-1}$
Herschel-Bulkley	$\eta=\tau_0/\dot{\gamma}+K\dot{\gamma}^{n-1}$
Casson	$\eta=\sqrt{(\tau_0/\dot{\gamma})^2+\eta_p^2}$
Cross	$\eta=\eta_{\infty}+(\eta_0-\eta_{\infty})/(1+(\dot{\gamma}/\dot{\gamma}_b)^n)$
Carreau	$\eta=\eta_{\infty}+(\eta_0-\eta_{\infty})/(1+(\dot{\gamma}/\dot{\gamma}_b)^2)^n/2$
Tscheuschner	$\eta=\eta_{\infty}+\tau_0/\dot{\gamma}+\eta_p/(\dot{\gamma}/\dot{\gamma}_b)^n$

Fig. 131 Mathematical model equations for describing flow behaviors as offered as alternatives for regression calculations.

Curve-fitting in this context means to "shrink" a more or less complicated shape of a flow- or viscosity curve to an equation defined by 2, 3 or even 4 coefficients. Curve-fitting has two advantages:

a.) In quality control it is easier to mathematically define tolerance ranges around standard regression coefficients than to optically compare various shapes of standard curves with any particular flow- and viscosity curve formed

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by measured test points. After one has programmed the actual acquisition of test data it is an obvious second step to continue with an automatic evaluation that answers the simple question: Is the tested material within or outside of the specification? Regression calculation helps to answer this question.

b.) Comparing test results gained by different rheometers often requires shear stress/viscosity values at specified shear rates which are most likely not identical with the shear rates of the data points of a steady-state flow curve. A regression calculation determining the best-fit equation will then allow one in seconds to calculate any intermediate shear stress/viscosity values needed for the comparison with other rheological data.

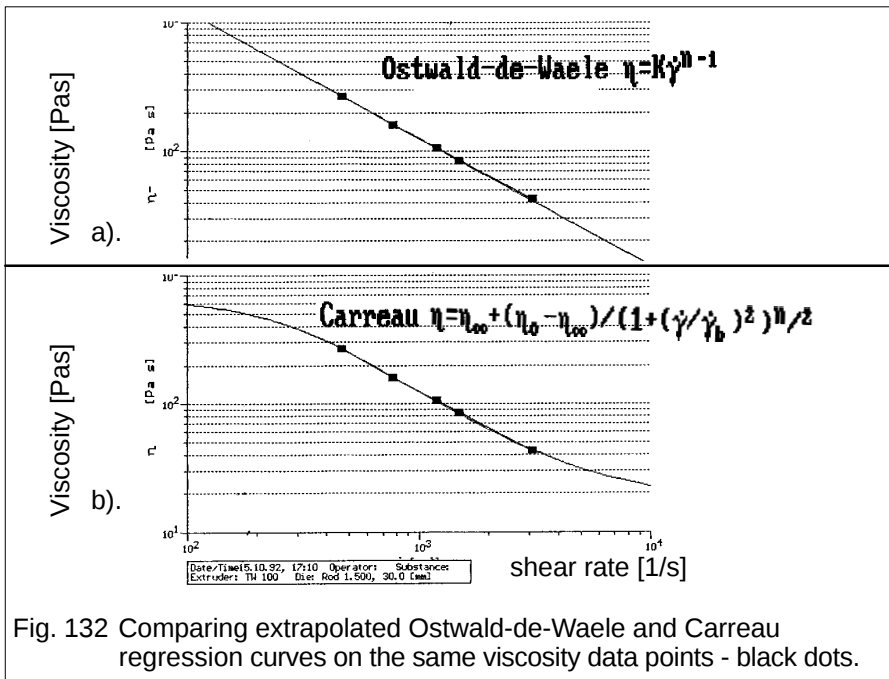


Fig. 132 Comparing extrapolated Ostwald-de-Waele and Carreau regression curves on the same viscosity data points - black dots.

It is common practice in industry to use the relatively simple Ostwald-de-Waele equation (power law equation) to describe the viscosity curve in a given shear rate range. This can be done by the determination of the 2 coefficients "K" and "n". Fig. 132a indicates that the Ostwald-de-Waele-regression curve provides in this particular case of a tested polyethylene a near perfect fit for viscosity data points within the given range of the measured points. This is not necessarily the case for all polymer melts, since even in double logarithmic scaling not all actually measured flow- and viscosity- curves are sufficiently straight to approximate them well using the Ostwald-de-Waele equation. For

this reason more rheological equations should be tried out for regression calculations.

The Ostwald-de-Waele regression curve in Fig. 132a being a straight line extends linearly beyond the range of the measured test points. It is obvious that this extrapolation to very low or very high shear rates will not be in line with the rheological reality i.e. the viscosity will always level off to a finite zero-shear viscosity η_0 . At very high – infinity – shear rates viscosity will asymptotically (second Newtonian region) approach a constant level of η_∞ . Rheologists have offered other regression equations to describe the flow behavior of particular polymer melts. The Carreau-equation which requires the determination of 4 coefficients has especially found wide acceptance. Using a computer this does not present a major problem. Fig.132b shows such a Carreau plot of the same η -data points as above.

9.4 The possible pitfalls of extrapolated regression curves.

Rheology is used to define for instance the melt flow behavior of polymers to characterize their processability, to give insights into the molecular structure, and to indicate influences related to polymer blending or compounding. Since polymer melt viscosity is always very shear rate sensitive one has to indicate the relevant shear rate range for a particular rheological problem. (See chapter 5 – Relevance of Shear Rates). Rheometer tests rarely provide viscosity data of acceptable significance for a shear rate range of more than two or three decades. Data over a much extended range might be necessary to describe particular processing conditions.

Extrapolation of a best-fit regression curve seems to be a very good, cost minimizing solution to measure viscosity data in a limited shear rate range and extrapolate to either higher or lower shear rates.

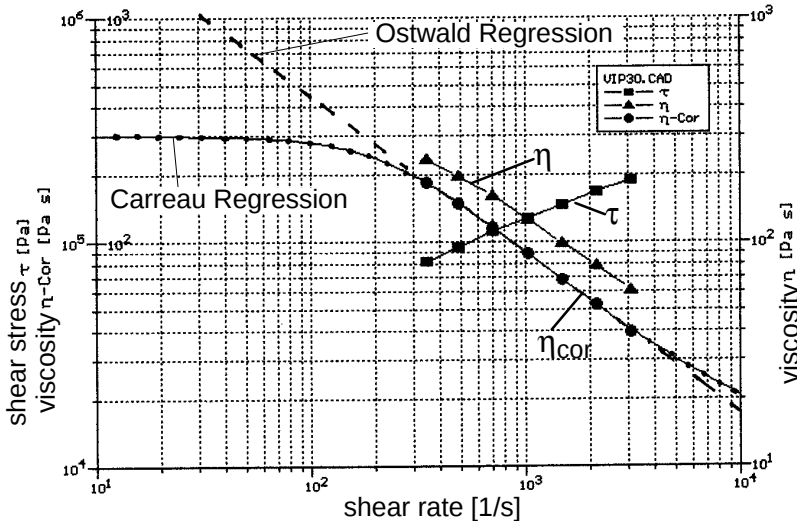


Fig. 133 Direct comparison of the extrapolated Ostwald-de-Waele- and the Carreau regression curves on the same data points η_{Cor} – black dots – which only cover a shear rate of one decade.

Fig. 133 shows flow and viscosity curves of a polyethylene melt tested using capillary rheometry with a rod-type capillary die. The viscosity data points $\eta \rightarrow$ triangles – were subjected to an Ostwald-de-Waele and a Carreau regression – $\eta_{Cor} \rightarrow$ black dots – for which the regression curves are also presented. While the Ostwald extrapolation beyond the range of the measured data obviously does not make sense, the Carreau regression calculation and the extrapolation to very low shear rates leads to a well defined zero-shear viscosity of $\eta_0 = 3 \cdot 10^5 Pa \cdot s$. It looks good on first sight. Some doubt is cast on the usefulness of this extrapolation by the statistical evaluation of the regression coefficients which the computer evaluation additionally provides: Values of uncertainty and the χ^2 which link, for example, the exponent n with an uncertainty of 20%.

The rod capillary tests of the polyethylene melt were extended by further slit capillary tests which provide data at shear rates about a decade lower than those gained by the chosen rod capillary.

Fig. 134 shows the combined viscosity test points of both the slit and the rod capillary test with all other extrusion parameters being the same. The Carreau regression equation on the rod capillary data which seemed so good in Fig. 133 is obviously very wrong with respect to the new Carreau regression

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calculation on the slit viscosity data and the extrapolation of the determined regression equation. The two zero-shear viscosity values η_{01} and η_{02} differ by a full decade of magnitude and most likely both are wrong!

As long as the viscosity curve is defined by measured data points in the shear thinning phase – the viscosity curve is characterized by an angle $\gg 0$ – the Carreau equation takes the last data points of the lowest and highest shear rates and bends the regression curves for lower and higher shear rates to parallel the abscissa $\rightarrow \eta_0$ and η_∞ . Adding more data points – as in this example with the slit capillary rheometer – changes the turning points of the regression curve and leads to new values of η_0 . To state the truth, the Carreau regression calculation also requires measured data points in the part of the viscosity curve in which even non-Newtonian liquids show a Newtonian flow behavior, e.g. their viscosity has become independent of shear rate.

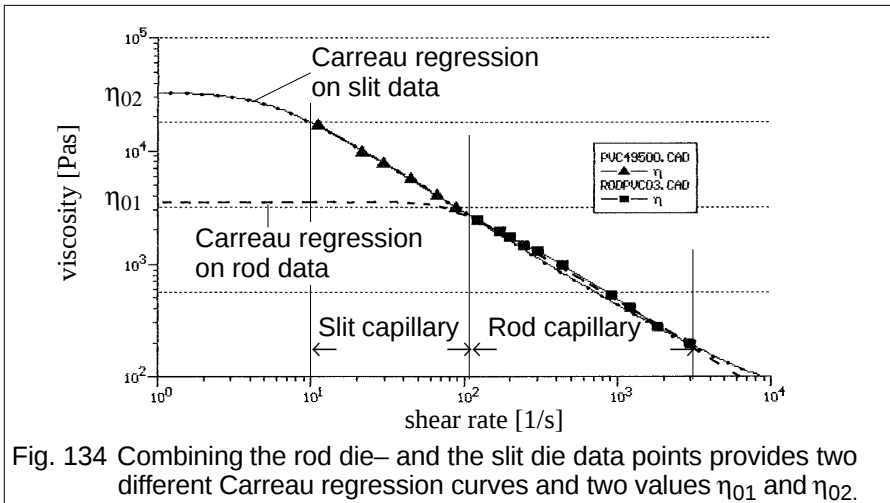


Fig. 134 Combining the rod die– and the slit die data points provides two different Carreau regression curves and two values η_{01} and η_{02} .

One might conclude from this example of an extrapolated evaluation that one should better do without. If one needs rheological information covering a very wide shear rate range then one will have to measure original data within that range. That will most likely require several tests with different rheometer dies or even the usage of types of rheometers such as CR- or CS-rotational viscometers (Fig. 85).

9.5 Corrections on measured “raw” data required as in the case of capillary rheometer results

9.5.1 The Bagley correction

The measured data obtained from capillary rheometers with **round capillaries** requires corrections with regard to entrance/exit effects which negatively influence the viscosity-related pressure loss. In these rheometers a pressure sensor is placed only in the entrance reservoir from which the melt is fed into the capillary which is small in diameter (D) but long in length (L) (Fig. 128 a).

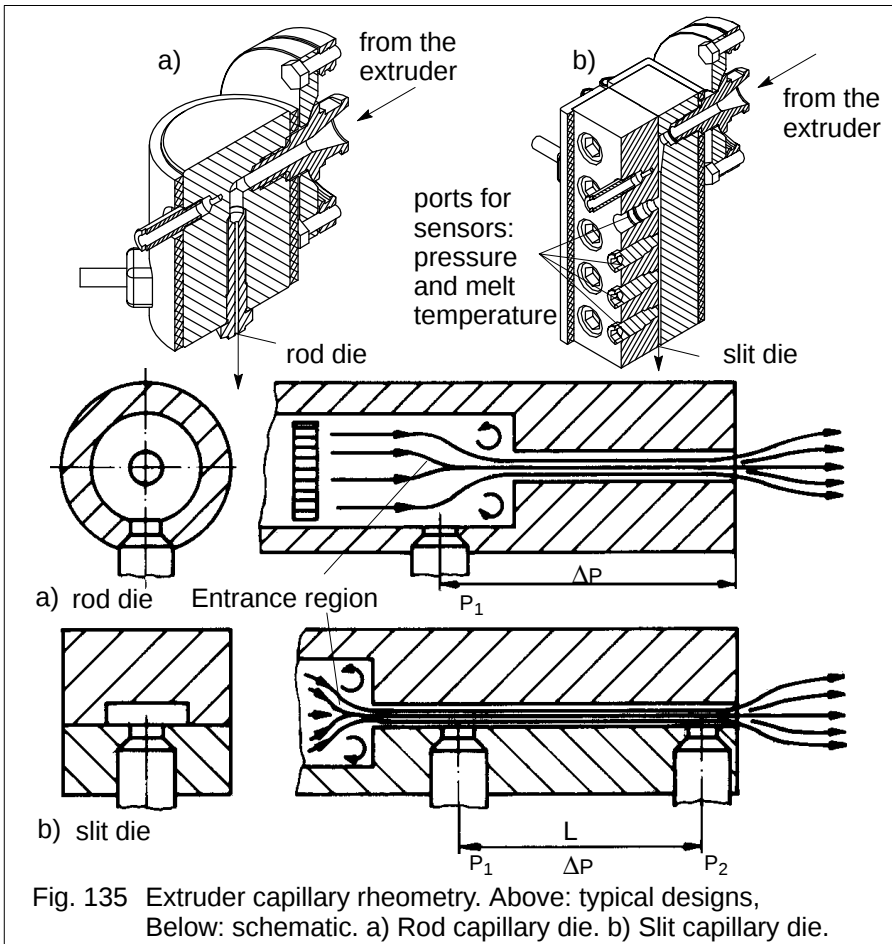


Fig. 135 Extruder capillary rheometry. Above: typical designs, Below: schematic. a) Rod capillary die. b) Slit capillary die.

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The capillary cross-section is so small that standard melt pressure sensors cannot be positioned inside of the capillaries with 1 or 2 mm diameter. The pressure loss required for the determination of the actual shear stress is under these test conditions determined only by the pressure difference between the pressure in the entrance of the capillary and the ambient pressure outside the capillary exit – Fig.135a.

This ΔP is not only caused by the resistance of the melt against the forced flow through the capillary, but also to a large extent by the energy/pressure loss resulting from:

a.) the unavoidable flow turbulence requiring more energy than laminar flow in the entrance region to the capillary, when the large diameter reservoir is almost stepwise changed to the small diameter capillary.

b.) The need to accelerate the mass from the low speed in the reservoir to the much higher flow speed through the rod capillary. Steady state flow conditions as required by the boundary conditions (see 2.9.2.) can only be assumed within the capillary itself.

c.) Another (often dominant) part of the entrance effect is linked to the elastic properties of the visco-elastic melt which temporarily absorbs and elastically stores some of the energy which is provided by the extrusion pressure to force the melt through the capillary. The absorbed part of this energy is fully recovered outside the capillary not having participated in the activation of the flow. It reappears when the extrudate having left the capillary exit is allowed to freely relax resulting in the phenomenon of die swell. Elasticity can also show-up as “melt-fracture” which leads to slip-stick effects in the die and to extrudates of very rough and non-uniform surface.

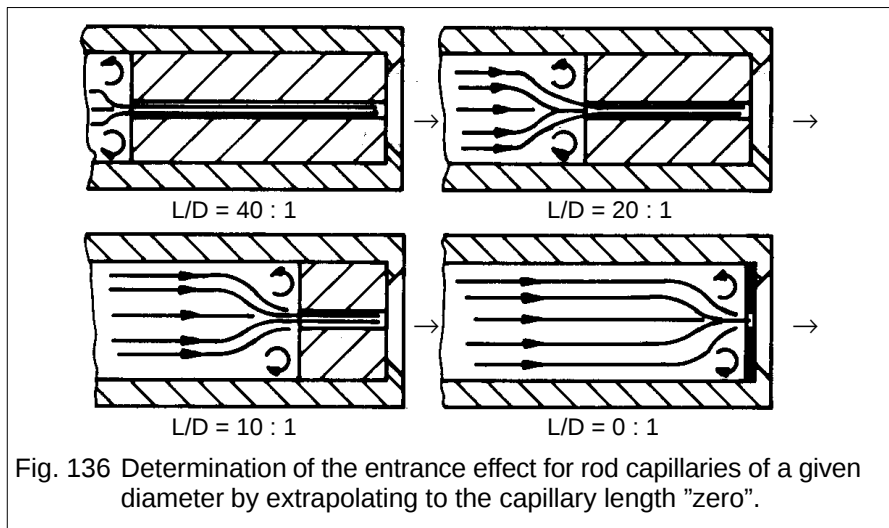
Entrance effects of this kind need not be accounted for when tests are run with slit capillaries wide enough to have standard size pressure sensors positioned flush with the slit (Fig. 135b). The actual pressure loss ΔP is then measured with at least 2 pressure sensors P_1 and P_2 placed at the distance L along the capillary length. In this test setup the first pressure sensor is installed far enough downstream from the capillary so that entrance pressure losses no longer interfere with the measured ΔP related to the flow along the capillary length segment L . Most good slit capillary rheometer dies have 3 pressure sensors equally spaced along the capillary to check whether the pressure drop is linear and to warn of faulty sensors. Any pressure reading which is obviously out of line with respect to the others may be an indication of such a faulty pressure sensor.

While slit capillary rheometers provide test results not requiring corrections related to entrance effects, they have limited use in tests which require high shear rates to simulate production processes such as flow-through nozzles in

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injection molding. Slit capillaries have relatively large cross-sections which for a given maximum pressure provided by a laboratory extruder lead only to low to medium shear rates as encountered in normal extrusion or compression molding. It is for this reason that rod capillary rheometers suitable for very high shear rates still occupy an important position in melt rheometry. Their test results should not be used without corrections for all the errors which can be termed "entrance effects".



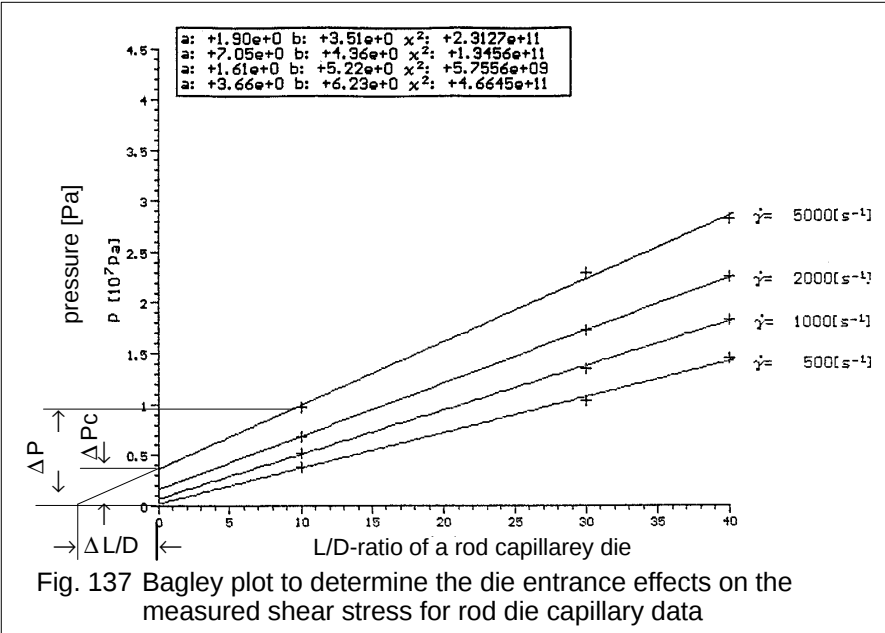
Mr. Bagley suggested a method for carrying out such a correction. His method requires running tests for a particular polymer with several dies, (at least 2), all having the same diameter (Fig. 136). All other test conditions are identical apart from the length/diameter ratios (L/D-ratio) of the dies, e.g. 10, 30 and 40.

Please note: the dies above are shown schematically with a 180° entrance angle. This angle should in fact vary with the rheological behavior of melts. Entrance angles of 90° are more common.

Tests with all of these dies have obviously the same entrance effect since the entrance region into the capillary is identical. The smaller the L/D-ratio of the die, the bigger the percentage of error involved due to entrance effects. One can extrapolate from dies with a high L/D-ratio to others with a smaller ratio by decreasing the die length L . This extrapolation will finally lead to a die which has just the entrance region but a die-length $L = 0$ or the L/D-ratio = 0. For such an extreme die the measured pressure loss will originate just from the total entrance effect which is to be determined.

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Bagley found that plotting the values ΔP for given shear rate levels gained in tests with several dies will provide a fan of straight lines in a diagram of ΔP versus the L/D -ratio (Fig. 137). These lines can be extrapolated to intersect with the ordinate at ΔP_c (c stands for correction). This is the pressure drop related to the entrance effect for a die with a capillary length of $L = 0$. Alternatively one can extrapolate the lines still further to intersect with the abscissa where negative values of L/D or a ΔL can be found, which when added to the actual capillary length L , would give a pressure loss which accounts for the entrance effect.

Correction of the shear stress value then means either subtracting the ΔP_c from the measured pressure loss " ΔP " or adding an imaginary additional length ΔL to the capillary length.

$$\tau_{\text{corrected}} = (\Delta P - \Delta P_c) \cdot \frac{R}{2L} \quad [71]$$

or

$$\tau_{\text{corrected}} = \Delta P \cdot \frac{R}{2(L + \Delta L)} \quad [72]$$

Fig. 137 is shown to indicate the magnitude of the Bagley correction on the measured raw data. For a die with an L/D -ratio = 10/1 and at a shear rate of $\dot{\gamma} = 5000 \text{ 1/s}$, a value of $\Delta P = 1 \cdot 10^7 \text{ Pa}$ is measured and one can read from

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the Bagley plot that the ΔP_c is about 40% of this ΔP . Thus the actual pressure loss to force the melt through the die or the shear stress that correlates to viscosity in this case is 40% lower than the uncorrected value. A Bagley correction results in a downwards shift of the shear stress ordinate.

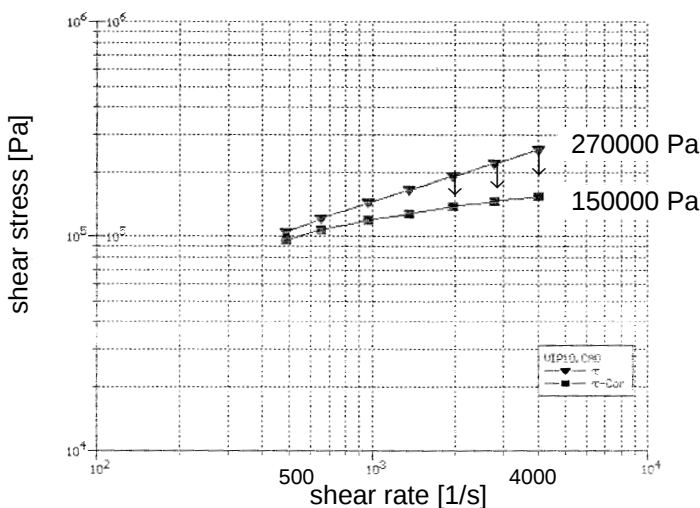


Fig. 138 Flow curves of tests with a rod capillary die showing apparent- and Bagley-corrected shear stress data points.

The Bagley correction of rod capillary data, when manually done, is more than troublesome and time-consuming. Computer software can automate this correction and do it in a minute or so in the following steps:

- The software takes the measured data of the pressure and flow rate for each of the three dies used and plots them. The data points of the three flow curves relate to different shear rates.
- An Ostwald-de-Waele regression calculation determines the relevant coefficients for each flow curve which are then used to calculate the corresponding pressure loss ΔP values for fixed shear rate values such as $\dot{\gamma} = 5000$, 2000 , 1000 and 500 1/s.
- They are then used to mark the data points for the three dies with an L/D ratio = $10/1$, $30/1$ and $40/1$ in the Bagley plot. Regression calculations for data points of equal shear rates allow the user to plot straight lines which connect the data points and which may be extrapolated to the ordinate or a negative intersect with the abscissa. This provides the values ΔP_c or ΔL .

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d.) They are then used to correct the shear stress data and this results in a corrected flow curve. At a shear rate $\dot{\gamma} = 4000 \text{ 1/s}$ and a die of a small ratio $L/D = 10/1$, the corrected value τ_{cor} is only 55% of the uncorrected value τ .

9.5.2 The Weissenberg-Rabinowitsch correction

The above mentioned Bagley correction is related to the geometry of rod capillary dies and to the quality of the pressure sensors to measure the relevant pressure losses. For rod **and** slit capillaries an additional correction related to the nature of the tested sample is required if non-Newtonian liquids are tested, i.e. all polymer melts. The relatively simple rheological equations for oils or water [Hagen-Poiseuille (pages 67/68)] must be corrected to take into account the particular relationship between the pressure applied and the resulting flow rate of fluids such as polymer melts. Being subjected to an unknown viscosity function, capillary rheometry provides "raw" data pairs of extrusion rate Q and the corresponding value of ΔP . Their mathematical treatment leads to the following equations.

The extrusion or flow rate $Q \text{ [m}^3\text{/s]}$ is defined as:

$$Q = \int_0^R 2 \cdot \pi \cdot r \cdot V(r) \cdot dr \quad [73]$$

r = radial coordinate within the limits of $0 < r < \text{capillary radius } R$

$V(r)$ = radial flow speed as a function of r

Partial integration leads to

$$Q = \pi r^2 V(r) \Big|_0^R - \int_0^R \pi \cdot r^2 \cdot \frac{dV}{dr} \cdot dr$$

For a further transformation one can use the following equation.

The shear stress is linearly changing with the radius r from its maximum τ_w at the outer wall to zero in the center of the capillary and this relationship is related to both Newtonian and non-Newtonian flow behavior:

$$\frac{\tau}{\tau_w} = \frac{r}{R}$$

or

$$\frac{d\tau}{\tau_w} = \frac{dr}{R} \longrightarrow dr = \frac{d\tau}{\tau_w} \cdot R$$

The shear rate is highly dependent on the non-Newtonian rheological characteristics of a fluid and therefore changes non-linearly with the radius r .

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The “true” shear rate $\dot{\gamma}_t$ as a function of r is:

$$\dot{\gamma}_t = - \frac{dV}{dr}$$

$$Q = \pi \cdot \frac{R^3}{\tau_w^3} \int_0^{\tau_w} \tau^2 \cdot \dot{\gamma}_t \cdot d\tau$$

For a Newtonian liquid with a viscosity η_N flowing through a capillary with a radius R and a length L , an apparent shear rate $\dot{\gamma}_a$ is given as:

$$\dot{\gamma}_a = \dot{\gamma}_N = \dot{\gamma}_t = \frac{4 \cdot Q}{\pi \cdot R^3}$$

The viscosity is
$$\eta_N = \frac{\pi \cdot R^4 \cdot \Delta P}{8 \cdot Q_a \cdot L} \quad [74] = [25]$$

It is known as the Hagen-Poiseuille equation.

The maximum flow speed at the center is:

$$v_{\max N} = \frac{\Delta P \cdot R^2}{4 \cdot \eta_N \cdot L}$$

The extrusion rate is:
$$Q_N = \frac{\pi R^4 \cdot \Delta P}{8 \cdot \eta_N \cdot L}$$

Combining the equations for flow rate and the apparent shear rate provides:

$$\frac{\pi \cdot R^3 \cdot \dot{\gamma}_a}{4} = \pi \cdot \frac{R^3}{\tau_w^3} \int_0^{\tau_w} \tau^2 \cdot \dot{\gamma}_t \cdot d\tau$$

$$\dot{\gamma}_a = \frac{4}{\tau_w^3} \int_0^{\tau_w} \tau^2 \cdot \dot{\gamma}_t \cdot d\tau$$

Differentiation of the above equation leads to:

$$\dot{\gamma}_t = \frac{3}{4} \cdot \dot{\gamma}_a + \frac{1}{4} \tau_w \cdot \frac{d\dot{\gamma}_a}{d\tau_w}$$

and its transformation:

$$\dot{\gamma}_t = \frac{\dot{\gamma}_a}{4} \left[3 + \frac{d \lg \dot{\gamma}_a}{d \lg \tau_w} \right]$$

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This equation can be shortened by defining:

$$s = \frac{d \lg \dot{\gamma}_a}{d \lg \tau_w}$$

It will reduce the above equation valid for rod capillaries to:

$$\dot{\gamma}_t = \frac{\dot{\gamma}_a}{4} (3 + s) \quad [75]$$

The equivalent for slit capillaries is:

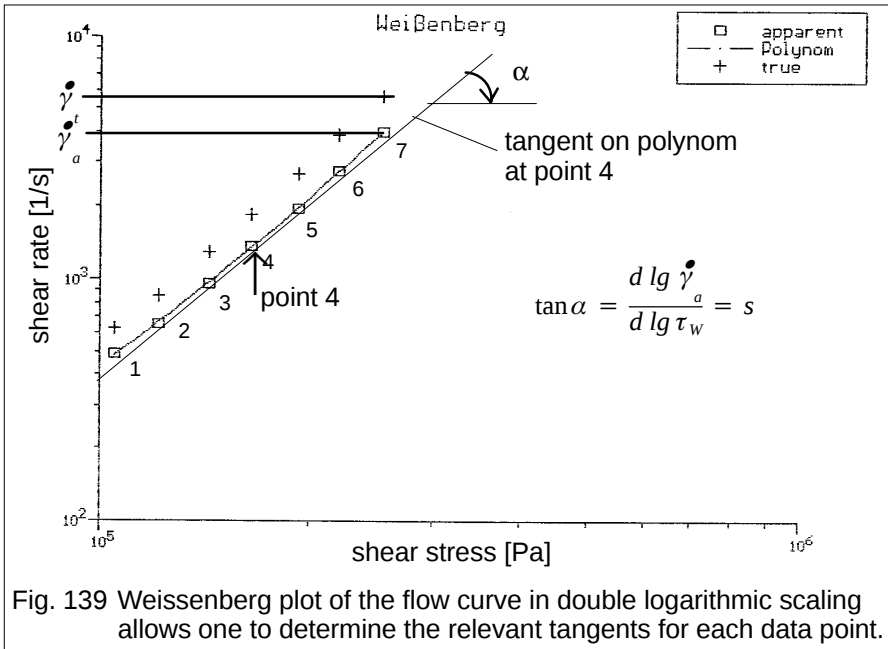
$$\dot{\gamma}_t = \frac{\dot{\gamma}_a}{3} (2 + s) \quad [76]$$

This means that the “true” shear rate $\dot{\gamma}_t$ can be found by correcting the “apparent” shear rate by a factor found by differentiating the shear rate versus shear stress curve plotted with double logarithmic scaling. This differential of the logarithmic curve represents the slope of that curve for a given apparent shear rate value. For pseudoplastic fluids the value of s will always exceed “1”. This means that for these liquids the true shear rate will always be greater than the apparent shear rate. For given shear stress values the corrected shear rate will then lead to corrected viscosity values less than the uncorrected ones.

Two rheologists Weissenberg and Rabinowitsch have introduced these equations into technical rheology for the correction of “apparent” rheometer data to “true” data. Evaluation of measured data from the testing of non-Newtonian fluids means plotting first the measured data in a diagram with double logarithmic scaling (see Fig. 139). Differentiation at any point of this curve is accomplished by curve-fitting on a segment of that curve defined by a number of adjacent data points with a polynomial function which may then be mathematically differentiated.

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Example:

Determination of the tangent on the test point 4 for the uncorrected curve in Fig. 132 is accomplished with the 3 preceding and the 3 following points i.e. points 1, 2, 3 and 5, 6, 7 are taken to find the suitable polynomial equation. One can then calculate in a second step the required differential “s” at point (4), which corresponds to the slope of the curve at point (4). This value “s” has a numerical value exceeding “1” which means that the true shear rate is always greater than the corresponding apparent shear rate (see the above equations [74] and [75]).

Having determined this shift factor s, the apparent shear rate values can be transformed point by point to their true values. This correction is in itself shear rate dependent.

The viscosity of a non-Newtonian fluid is then:

$$\eta = \frac{\tau}{\dot{\gamma}_t}$$

$$\frac{1}{\eta_t} = \frac{4}{\tau_w^4} \int_0^{\tau_w} \frac{\tau^3}{\eta} \cdot d\tau$$

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This integral can be solved for fluids such as most polymer melts which fit the Ostwald-de-Waele equation (power-law equation) which is characterized by the exponent “n”. This leads to:

$$\eta_t = \eta_a \frac{4 \cdot n}{3n + 1} \quad [77]$$

For $n = 1$ (Newtonian liquid) it reduces to:

$$\eta_t = \eta_a$$

For non-Newtonian liquids with lower values of n :

$$n = 0.8 \quad \longrightarrow \quad \eta_t = 0.94 \cdot \eta_a$$

$$n = 0.6 \quad \longrightarrow \quad \eta_t = 0.85 \cdot \eta_a$$

$$n = 0.4 \quad \longrightarrow \quad \eta_t = 0.73 \cdot \eta_a$$

$$n = 0.3 \quad \longrightarrow \quad \eta_t = 0.63 \cdot \eta_a$$

this is 37% below the η_N !

For $n = 1$ the true and apparent viscosity values are identical. For $n = 0.4$, (which is quite a normal value for e.g. polyethylene melts), the true viscosity is only 73% of the apparent viscosity. Working with uncorrected shear rates and viscosities lead to very sizable deviations from the true values of most polymer melts. Modern computer software makes the Weissenberg-Rabinowitsch correction – which manually performed is more than troublesome – something that requires only a minute or two – even for people without a university degree.

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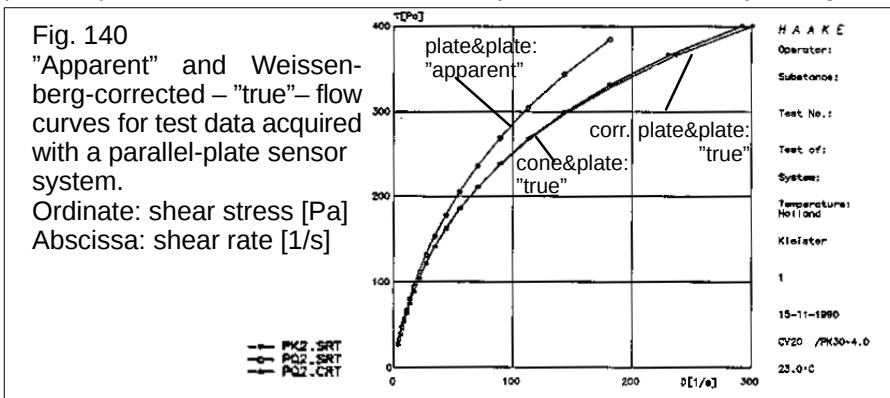
9.5.3 A short summary of the principles behind corrections on raw data

- Corrections are a “must” if the rheological test data is to be used for the design of machinery and pipe lines, and if someone needs to compare results measured with different rheometers. The corrections are not “peanuts” but often have the same magnitude as the measured values.
- Corrections are related to the test geometry and to the particular flow behavior of the tested samples. The more non-Newtonian a sample is, the more important is the correction.
- Rod capillary tests require **both** the Bagley **and** the Weissenberg-Rabinowitsch corrections, while only the latter is necessary for slit capillary tests.
- Not only capillary rheometer data of non-Newtonian fluids requires a Weissenberg-Rabinowitsch correction, but also those of parallel-plate sensor systems of rotational rheometers. This type of sensor system does not provide a constant shear rate for a given rotor speed as is the case of the cone-and-plate sensor systems. Its shear rate increases with the radius from zero at $r = 0$ to a maximum at the outer rim ($r = R$) of the rotating plate (page 50). It is common to use the maximum shear rate at $r = R$, but the resulting viscosity data is **apparent** data which also requires a correction taking into account how much the fluid deviates from Newtonian behavior. Again soft-ware facilitates this correction.

$$\eta_{\text{true}} = \tau_{\text{apparent at } R} / \dot{\gamma}_R \left[(3 + n) / 4 \right] \text{ for Ostwald-de-Waele substances}$$

n = exponent of power law equation
 η_t = true or corrected viscosity
 τ_a = apparent shear stress at radius R

Fig. 140 indicates flow curves of a glue tested with both a cone-and-plate- and a parallel-plate sensor system. Only a correction of the parallel-plate data brings it in line with the cone-and-plate data. The Weissenberg correction on parallel-plate shear stress data results in quite sizeable viscosity changes.



9.6 The "WLF"–time-temperature superposition

When testing fluids dynamically in CS-rotational rheometers equipped with parallel-plate-, cone-and-plate-, and coaxial cylinder-sensor systems, stresses will be imposed in a sinusoidal time pattern. The measured strain and phase shift data can then be transformed to the storage modulus G' , the loss modulus G'' , the complex viscosity η^* etc. all as functions of frequency ω . Modern rheometers are designed to cover within reasonable time spans with one particular sensor system – one particular sensor geometry – a frequency range that rarely exceeds much more than 3 decades: i.e. $\omega=0.01$ to 10 1/s. (Technically the min/max values for rheometers are normally $\omega=0.001/100$ 1/s).

Limitations in practical rheometry normally come from the fact that “super-long” test times will not even be acceptable in basic research applications. Another limitation can be that samples at low temperatures become so highly viscous that their viscosity can no longer be measured with an existing rheometer.

Those who need test data to explore the rheological influence of fillers in gum-type pastes at shear rates as low as 10^{-4} 1/s have to wait some 3 hours. Those who require data at $\omega=10^{-5}$ 1/s will get the first measurement point after some 24 hours and complete G' and G'' /frequency curves not before the end of two days. It is safe to assume that testing times of this length are not practical.

The reaction of visco-elastic fluids to sinusoidally imposed shear stresses is related to the mobility of molecules and volume elements within such a sample. This mobility, also characterized by the relaxation time spectrum, is related to the type of the major fluid component but also to the type and percentage of all other ingredients of a particular material. At low temperatures this mobility is small so that the reaction of such a fluid is slow. If one raises the temperature, the molecular mobility is increased so that one can explore the effect of enclosed filler aggregates or rubbery volume elements in a thermoplastic melt by means of higher and faster responses in the visco-elastic fluid. A strong, fluid specific correlation between the time of response related to the material functions at the measured frequencies and the temperature, at which samples are rheologically measured, exists.

This interdependence was explored as early as 1955 by M. L. Williams, R.F. Landel and J.D. Ferry who provided a theoretical understanding of the temperature dependence of the physical structure of the fluids. They tested polymer samples at temperatures 50 to 100°C above their glass transition temperature T_g in steady shear and in dynamic tests. This leads for each temperature value to a set of curves of i.e. G' , G'' or the phase-shift-angle δ as a function of angular velocity. These material functions can span 2 to 3 decades for a given temperature range of some 50°C– Fig. 141. The resulting

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curves of a particular rheological material function such as the storage modulus G' will form a temperature-related set of curves within a G' /frequency diagram with the curve at lowest temperature being positioned highest. These curves differ not only in their vertical position but also in their shapes which gradually change with temperature.

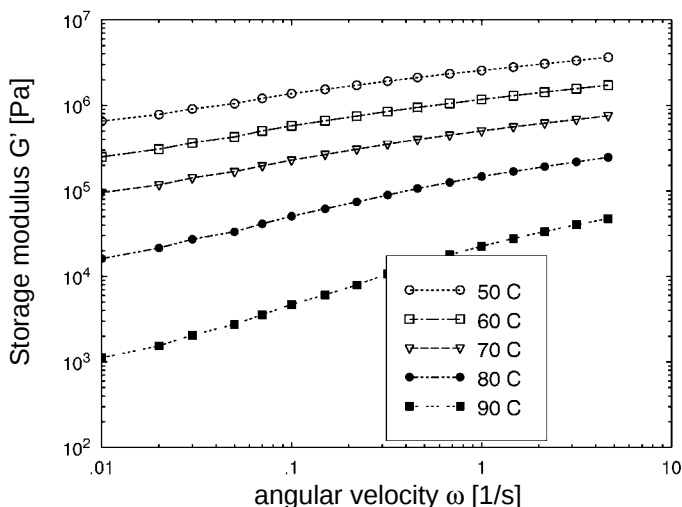


Fig. 141 CS-rheometer RheoStress RS100: Dynamic testing of a chewing gum mass at variable test temperatures.

The three authors realized that one may shift the curves of this family horizontally – along the frequency/angular velocity abscissa – and perhaps also vertically so that all curves form a single master curve for a reference temperature. If the reference temperature is chosen to be in the middle of the chosen measuring temperatures then the curves at test temperatures below the reference temperature are shifted to the right, i.e. to higher frequencies until the ends of adjacent temperature curves just meet or partially overlap. Similarly test curves of higher than the reference temperature are shifted to the left. This “master curve” formed by this combination or “superposition” then covers a frequency range that significantly increases the range of the actually measured, temperature related curves. An example of such a diagram with “manually” shifted curves is presented in Fig. 142, while Fig. 143 shows an example of a computerized evaluation of 3 master curves.

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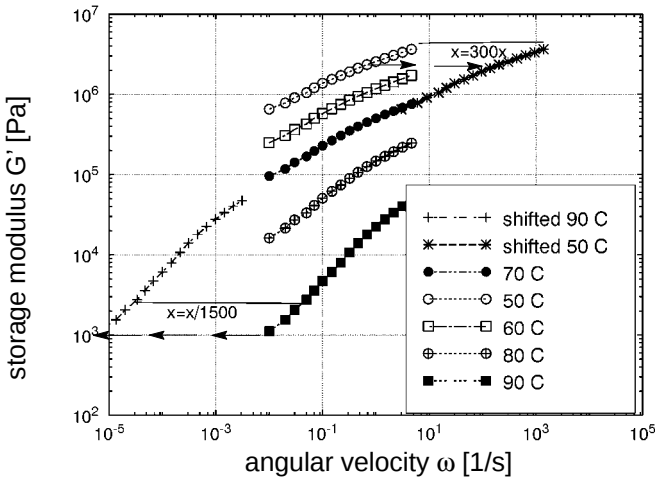


Fig. 142 Dynamic testing with a CS-rheometer: Shifting curves related to different test temperatures to form a master-curve covering an extended range of angular velocity ω .

Providing test data for a given material function within a limited frequency range at variable temperatures and the curve shift that follows leads to extended ranges of reaction times or frequencies. This data transformation is known as the "time-temperature superposition" and it is linked to the names of those scientists Williams, Landel and Ferry who backed the empirical curve shift procedure by a scientifically based theory: WLF.

When measuring at different temperatures within a range not exceeding 50°C the shift of measured curves – in the example of Fig. 143 of $G'/\text{frequency}$ – will lead to rheological data by means of the master curves that can easily cover an 8 decade frequency range which otherwise cannot be explored.

The actual testing, that can lead to such a master curve, will require normally not more than a single hour for both the warming-up-phases to 5 increasing test temperatures and the subsequent tests at each temperature level. The computerized shift procedure with the HAAKE WLF-software and a modern computer requires only a minute or two. The total test and evaluation time for this time-temperature superposition is then about a 1/10 to 1/20 of the time that an actually measured, wide frequency master curve would require – if an actual testing was at all possible.

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The computer software for the WLF superposition works in two steps.

1). It determines automatically how much the temperature related curve segments must be shifted horizontally – shift factor $a(T)$ – and/or vertically – shift factor $b(T)$ – to form a continuous master curve at the reference temperature.

$$\omega(T) = a(T) \cdot \omega(T_0)$$

$a(T)$ = horizontal shift factor

$\omega(T)$ = frequency at a freely chosen temperature T

$\omega(T_0)$ = frequency at the reference temperature T_0 .

Since the frequency ω is linked to the relaxation time λ of the fluid, the above equation can be rewritten:

$$1/\lambda(T) = a(T) \cdot 1/\lambda(T_0)$$

It indicates what the deformation-time-response is with respect to the complex modulus G^* . The phase shift angle that marks the response or relaxation times of fluids is related to temperature changes.

For samples that show large density differences it may be required to shift individual measured curves not only horizontally but also vertically by means of the shift factor $b(T)$.

Having measured G' -data one can write:

$$G'(T) = b(T) \cdot G'(T_0)$$

T being again the freely chosen temperature and T_0 the reference temperature. The shift factor $b(T)$ of most fluids is close to “1”. It is therefore decades apart from the value $a(T)$ and it may then be neglected.

2.) Plotting the actually determined shift factors $a(T)$ and $b(T)$ as a function of temperature provides curves for which a regression calculation will lead to a fitting mathematical equation. It can then be used to determine the shift factors for any intermediate temperature and for the master curves of the material functions such as G' , G'' , η^* or η' at that reference temperature.

This time-temperature superposition allows one to explore fluids rheologically in frequency ranges which are otherwise not possible, neither technically nor time-wise. But one has to keep in mind that the measured curves within the whole temperature range only gradually change with temperature, i.e. the rheological behavior does not change abruptly as is the case close to the glass-transition temperature. At T_g the mobility of molecules changes drastically. It therefore would not make sense to “extrapolate” from curves below T_g to those above. The shift factor $a(T)$ found for a particular fluid will relate mainly to the response time – “internal clock” – of the dominant matrix material of the fluid. In polymer blends the major blend polymers should have similar response times in order to determine one meaningful $a(T)$. Shift factors of compounds with a high percentage of filler basically different from the matrix material should be critically checked.

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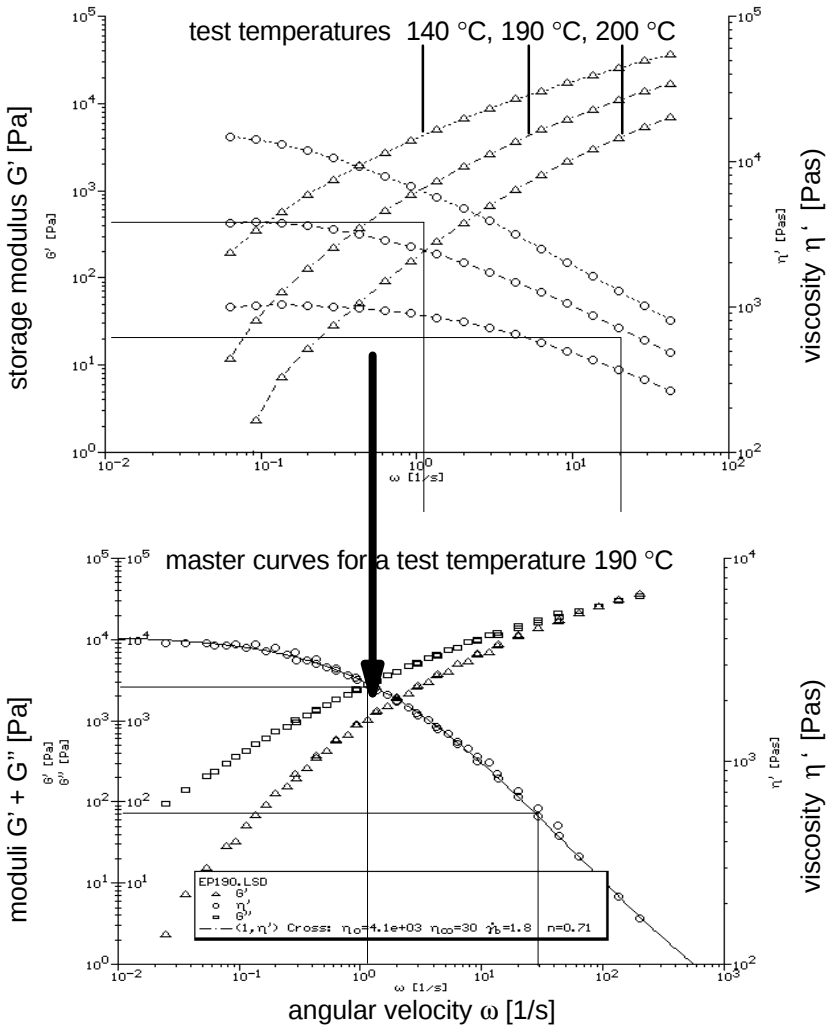


Fig. 143 Master-curves of η' , G' and G'' determined by the time-temperature-superposition of dynamic test data of a polyethylene melt measured at variable temperatures.

When discussing master curves, one must not neglect the fact that at the ends of the extended frequency ranges, the level of tolerance or the significance of the mathematically determined data is reduced in comparison to actually measured data.

9.7 Evaluation of the long-term viscous and elastic response of a polyethylene melt in a CS-rheometer creep and recovery test

These tests are designed to define the long-term – minutes or hours – behavior of visco-elastic materials.

A sample of HDPE-melt (Fig.144) was subjected in an initial test-phase of $t_1=100$ s to stresses in increasing order causing strains which equally increase. In this context it was tested in a second test-phase of $t_2=200$ s to see how much and how fast these strains will decay once the applied stress has been removed. While in the first phase one part of the applied stress was elastically stored and the other was used to initiate viscous flow – the magnitude of these parts with respect to each other is unknown until equilibrium is attained –, the elastic and the viscous components in the rheological behavior can be distinguished during the second recovery phase.

Please note:

When an outside stress is applied on a polymer specimen – i.e. it is compressed or twisted- and the load is maintained long-term, the internal stress in the specimen can **relax**: the stress is relieved internally due to microflow of molecules. One can determine the relaxation time λ for the stress to relax to a fraction $1/e$ of the initial stress value – with $e=2.73$.

When an outside stress is applied on a polymer specimen – it is compressed or twisted and at time t_1 the applied stress is fully removed stepwise the specimen can **retard**. In creep and recovery testing the recovery phase of a sample is under this definition a retardation process of the internal stress release. This process may be subjected to a "retardation time spectrum".

The elastically stored deformation energy will reduce the maximum strain of the first creep phase. The recovery curve of the second phase will drop towards the abscissa and eventually reach a constant strain level. The difference between the strain maximum and this constant recovery strain level is the elastic recovery of the tested material. The difference between that constant recovery strain level and the abscissa describes the amount of unrecoverable strain corresponding to viscous flow.

Fig. 144 indicates that with increasing stress in the first phase the recovery also increases. For the stress of 500 Pa the recovery is approximately 25 % after 200 s (some 3 min). The slope of the recovery curve has not reached yet a constant level, i.e. a parallel line to the abscissa. One may expect that the ratio viscosity/elasticity will still change further with time.

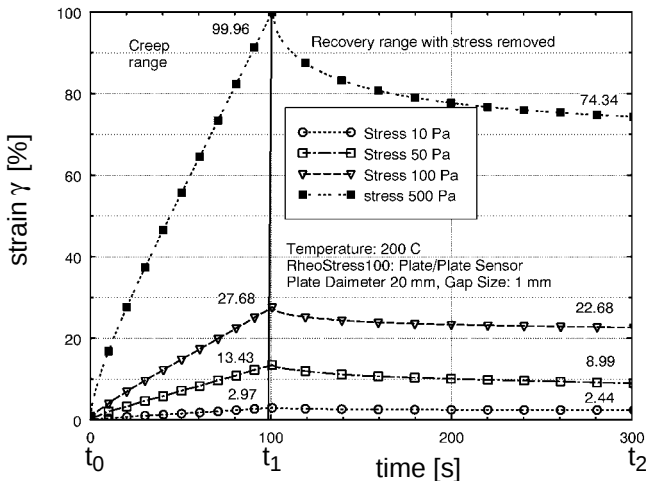


Fig. 144 CS-rheometer RheoStress RS100: Creep and recovery curves of a HDPE melt subjected to 4 stresses.

It has been indicated (see 4.3.3.2.) that visco-elastic samples normally require longer recovery/retardation times than the 3 min which were allowed in the tests for which data is reported. It is of interest to assess how far the sample might have recovered had the recovery time been longer or even infinite. Rheology provides mathematical models dealing with retardation phenomena, which describe the strain decay in visco-elastic samples. This decay is then defined by a characteristic relaxation time “ λ ” that can be compared to a model substance with a dashpot/spring combination. Most polymer melts, especially blends or compounds with fillers of any type or shape, cannot be represented by just a single dashpot/spring-combination but by many of these elements in series or in parallel. This will then result in a recovery process which can only be described by a “retardation time spectrum” with more than one time value λ .

In Fig. 145 the result of a regression calculation with an equation utilizing 3 retardation times is shown. The equation which is curve-fitting for $t_2 - t_1 = 200$ s of the recovery period is extrapolated to provide a regression curve that extends to 1000 s. This equals a recovery time of over 15 min:

The computer prints the equation used in Fig. 138 as:

$$y = a + b \cdot \exp(-x/c) + d \cdot \exp(-x/e) + f \cdot \exp(-x/g)$$

In the equation are:

y = strain value as a function of time x

a = strain value that is reached at the time $x = \text{infinity} \rightarrow$ hours, days:

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"a" represents the viscous part of the rheological behavior of the sample, i.e. the non-reversible part of the deformation related to viscous flow during the first testing phase.

c, e, g = retardation times $\lambda_1, \lambda_2, \lambda_3$ c = 7.2; e = 22.3; g = 219.5
b, d, f = material coefficients.

Please note: after a 3 min recovery the recovered elasticity was about 25%. Extrapolating the measured recovery curve with the above equation and the evaluated coefficients indicates that during a total recovery time of 15 min the viscosity/elasticity ratio is no longer 75/25 but has changed to 68/32. Using this equation still further to perhaps 10000 s recovery time will show only a very marginal further change.

It is certainly best if one runs tests as long as it seems necessary even if it takes hours or even days. High molecular weight polymers require very sizeable recovery times and just 3 min may not be sufficient or even lead to wrong results if for some types of polymers their short-term- and long-term-behavior crosses over. In such a case a simple extrapolation can lead to very misleading interpretations and predictions. A mathematical treatment of sufficient measured data can keep the testing time within reasonable limits.

It may be worthwhile to note that the above regression calculation required a sophisticated data processing so that even a computer with a 486-processor requires some 2–3 min and one with a 386 processor may take up to 30 min.

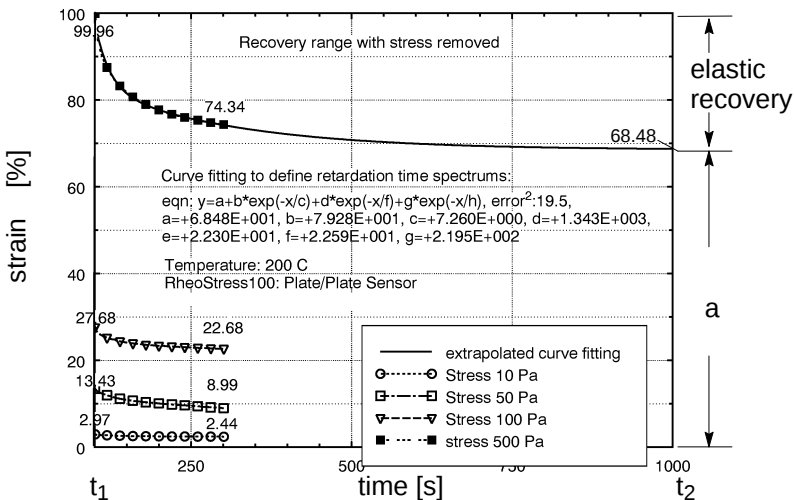


Fig. 145 Extrapolating the regression curve to longer retardation times

9.8 Mathematical treatment of test results in retrospect

For those who still remember using pocket slide-rules for calculating the shear stress, the shear rate and the viscosity, modern computerization still has the aura of a “miracle”. We can do now-a-days much more – see the WLF-Superposition – and much faster. Computers allow us to evaluate dynamic data and thus establish the interdependence of viscosity and elasticity, and provide a long-time differentiation between elastic and viscous responses in creep and recovery tests. We can present data in tabulated and graphical form and we can evaluate the significance of data to allow a better interpretation of results.

But results are still dependent on the operator’s ability to provide optimum test conditions. One must be aware of the pitfalls of turbulence, non-linear viscoelasticity or of plug flow. While tests using computers can be so fully automated that one could think of reading a newspaper while the rheometer and computer do their work, it is still correct procedure to keep an eye on the extrudate at the die or the sample sheared in a cone-and-plate sensor system – **at least** when establishing a quality control test procedure for the first time for samples or batches which are known not to differ too much in the long-term.

10. Relative Polymer Rheometry: Torque Rheometers with Mixer Sensors

10.1 Preliminary remarks

The previous chapters have dealt predominantly with absolute rheometry which relates the measured viscosity and elasticity data to absolute units of physics: force, length and time. Having accepted very strict test conditions with respect to the instrument geometry and the testing program within the limits of the “boundary conditions”, the results can be given in the internationally accepted units of “Pascal seconds” – Pas or mPas. It is the advantage of absolute rheometry that it characterizes samples objectively, and independent of the particular test equipment and its manufacturer.

Relative rheometry simulates – as in the case of torque rheometers with mixer sensors – real life process conditions as they are found in small or large internal production mixers or extruders. Torque rheometers with mixer sensors (Fig. 146) are based on a totally different concept in comparison to absolute rotational rheometers: They make use of miniature internal mixer sensors, which are down-scaled counterparts of large production mixers.

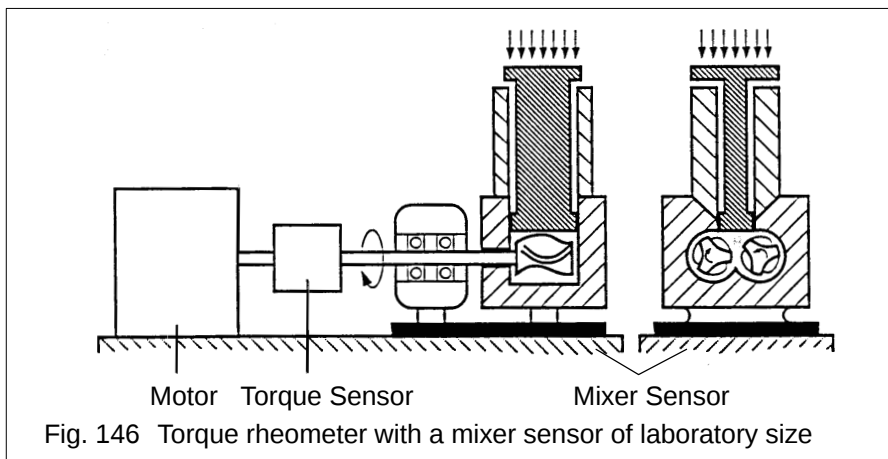


Fig. 146 Torque rheometer with a mixer sensor of laboratory size

They are designed to create as much turbulent flow and high shear action as possible to provide an optimal mixing of all the heterogeneous components of i.e. polymer melts or rubber compounds under process conditions which provide non-linear visco-elastic responses of the highly sheared materials. The resistance of the test sample against being mixed is proportional to its viscosity and it is measured in a torque rheometer as the reactionary torque on the rotors. This torque is normally recorded as a function of time. The graphs of torque versus time are named “rheograms”

10.2 Assessing shear rates in mixer sensors.

Mixer sensors consist of a temperature controlled mixing chamber and two rotors aligned parallel and at some distance to each other. The circles of the rotor actions are just touching each other. These rotors counter-rotate at a speed ratio of e.g. 3:2. For example: the drive speed of the torque rheometer and of the left rotor is 90 rpm, while the right rotor rotates at 60 rpm. (Some special mixers found in the rubber industry make use of speed ratio of e.g. 8:7). The left rotor normally rotates clockwise and the right rotor anti-clockwise. The shape of the rotors – roller blade, cam blade, Banbury blade, or sigma blade rotors – are designed to provide together with the established speed ratio an optimal mixing both radially and axially.

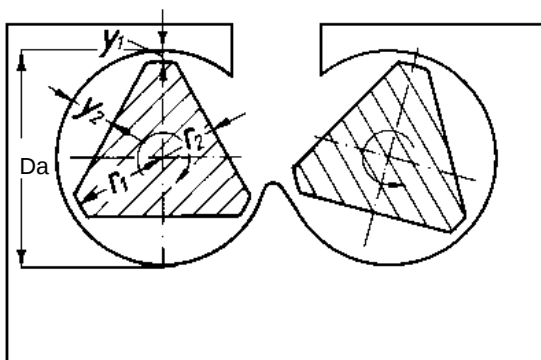


Fig.147 Cross-section of a laboratory-size mixer sensor to define dimensions

Polymer melts and rubber compounds are highly non-Newtonian, i.e. their viscosity depends on the applied shear rate, which can be adjusted on torque rheometers by means of a variation of the drive/rotor speed. While a defined shear rate for flow in mixers cannot be given, it seems worthwhile to consider the magnitude of the mixer shear rates within the total range which can be relevant for polymer processing – Fig. 84

The special shapes of the rotors – not mathematically defined but empirically found – and the chosen speed ratio provide a very complex flow pattern in the radial and axial directions and especially in the middle of the mixing chamber above its saddle where the masses drawn by the two rotors towards the center are forcibly intermeshed. To get some idea of a relevant shear rate range one can assess the minimum and maximum gap sizes between the rotors and the mixing chamber together with the tangential speeds on the left and the right

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rotor related to a typical drive speed. These data allow one to calculate for the radial flow minimum and maximum shear rates and their ratio.

Typical dimensions of such a laboratory mixer are:

Radius of the mixing chamber	$R_a = Da/2$	= 19.65 mm
Largest rotor radius	r_1	= 18.2 mm
Smallest rotor radius	r_2	= 11.0 mm
Widest gap size	y_2	= 8.6 mm
Smallest gap size	y_1	= 1.4 mm

v_1 = tangential speed at the radius r_1 .

The smallest gap y_1 between the left-side rotor and bowl chamber wall provides the maximum shear rate = $\dot{\gamma}_1$.

The widest gap y_2 between the left-side rotor and the bowl chamber wall provides the minimum shear rate = $\dot{\gamma}_2$.

Calculation of the shear rate range encountered in a mixer:

Largest shear rate	$\dot{\gamma}_1 = v_1/y_1$
Smallest shear rate	$\dot{\gamma}_2 = v_2/y_2$
Assumed rotor speed	$n_{11} = 90 \text{ 1/min}$

This is equal to : $n_{12} = n_{11}/60 \text{ 1/s} = 1.5 \text{ 1/s}$

$$\dot{\gamma}_1 = 2 \cdot r_1 \cdot \pi \cdot n_{12}/y_1 = (2 \cdot 18.2 \cdot 3.14 \cdot 1.5/1.4) = 122.5 \text{ 1/s}$$

$$\dot{\gamma}_2 = 2 \cdot r_2 \cdot \pi \cdot n_{12}/y_2 = (2 \cdot 11.0 \cdot 3.14 \cdot 1.5/8.6) = 12.05 \text{ 1/s}.$$

The comparable shear rates on the right-side rotor rotating with a rotor speed $n_{21} = 0.66 \cdot n_{11} \text{ 1/min}$ are:

$$\dot{\gamma}_3 = 81.6 \text{ 1/s} \quad \text{and} \quad \dot{\gamma}_4 = 8.03 \text{ 1/s}$$

Thus the shear rate ratio on the left-side rotor is:

$$\dot{\gamma}_1 / \dot{\gamma}_2 = 122.5 / 12.05 \approx 10$$

The comparable shear rate ratio on the right-side rotor is:

$$\dot{\gamma}_3 / \dot{\gamma}_4 = 81.6 / 8.03 \approx 10$$

For a preset rotor speed of $n_{11} = 90 \text{ 1/min}$ the maximum shear rate ratio for both left and right rotor is:

$$\dot{\gamma}_1 / \dot{\gamma}_4 = 122.5 / 8.03 \approx 15$$

Taking the example of Fig.85 with the viscosity curves of polyethylenes the above ratio means that the corresponding viscosities for the shear rates of $\dot{\gamma} = 10$ and 150 1/s are not just a few percent but more than a decade apart. If one follows this argument then one can assume different spots within the

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mixing chamber for which volume elements are characterized by considerably different viscosities. While no exact shear rates can be given for the flow in large and laboratory-size mixers it is safe to assume a relevant mean shear rate which correlates in units of (1/s) to the chosen rotor speed in units of (1/min). The measured torque is then proportional to a corresponding mean viscosity of the tested material.

A conversion of torque data of mixer sensors to absolute viscosity data given in units of Pas or mPas does not make sense for samples which are almost always highly non-Newtonian and therefore require exact shear rates to make viscosity data meaningful. This should not be considered as a criticism of mixer tests – they can provide important information on processability of many materials which absolute rheometry cannot. In fact both absolute and relative rheometry should be considered as synergistic to each other. Their benefits and limitations in different areas will together describe materials in a much broader sense which each of the two alone cannot provide.

10.3 The relevance of relative torque rheometer data.

Mixer test results are relative. The complicated shape of the mixing chambers and of the rotors and the temperature control makes test results of several samples only directly comparable to those of mixer sensors of a particular size and a particular manufacturer: data are therefore obviously not “absolute”. Samples having been tested in mixer sensors are graded in relation to “standard”-materials which are known to perform well or badly in specific production processes or as finished products in their application. Relative rheometer test results in graphical or tabulated form are not “worth the paper” they are plotted or printed on, unless it can be proven, that the quality ranking of materials with respect to their processibility or their performance in application is duplicated by the ranking of the mixer test data. Anyone who starts to use torque rheometers with mixers will have to first establish matrix tables of experimental data on the performance of materials and compounds in production processes versus the mixer sensor data with parameters such as: test temperature, rotor speeds, length of shear time, sample volume, ratio and type of the blend polymers, types and percentages of all ingredients in the sample etc.

“Standard materials” – i.e. in production machinery well-performing materials – provide “standard rheograms”. In quality control the deviation of batch rheograms from the standard rheograms is the “test result”. Varying one test parameter at a time such as the type of resin, its particle size distribution or the percentage of a lubricant influencing e.g. the rate of melting of a PVC-dry-blend will indicate how much and in which direction these modifications will change a PVC-compound's ability to melt. Interpreting torque rheometer data is an “art” requiring a lot of experimental data and a lot of operator experience – but some 10000 torque rheometers being used for decades worldwide have proven that this concept of relative rheometry has great practical and economic merits inasmuch as it drastically reduces time for trial runs on large production machines and saves tons of materials otherwise consumed in these large scale processibility tests.

10.4 Rheograms – Fig. 148

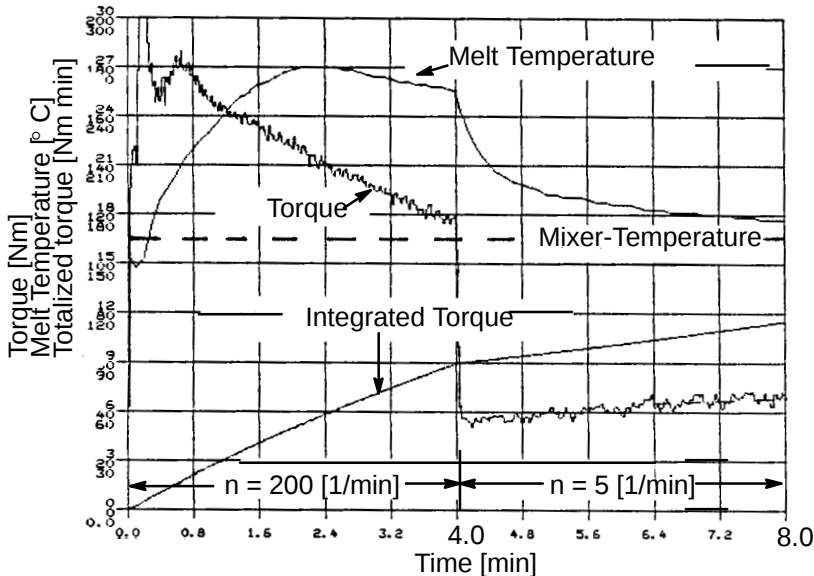


Fig.148 Rheocord90: Typical mixer test results plotting torque/viscosity, melt temperature and mixing energy/totalized torque as a function of the time of testing.

Rheograms – Fig. 148 – are primarily graphs of torque versus test time. They characterize the rheological changes of a sample during melting, during incorporation of fillers such as carbon black, during absorption of oils or plasticizers in carbon black or PVC-powders, and during processes such as viscosity decreasing degradation or viscosity increasing molecular cross-linking. Mixing is normally carried out at high shear rates/high rotor speeds and this leads to shear heating within the tested sample raising the melt temperature sometimes 30 or even 40°C above the preset temperature of the mixer. No ideally designed temperature control of electrically heated and air cooled mixer sensors nor a thermal liquid heating/cooling by means of external baths and circulators can keep both mixer and melt temperature the same for tests at high shear. Two samples which differ much in their viscosity will result in rheograms with both torque **and** melt temperature curves being different making it difficult to directly compare them. To facilitate such a comparison it is a good procedure to program the test in such a way that the test phase at high shear is automatically followed by a second phase at low shear: With a now very much reduced shear heating the melt temperature will gradually approach the lower preset temperature level of the mixer. The decrease of the

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melt temperature, of course, results in an increase of the torque/viscosity curve. On this common temperature basis it is then possible to compare the torque/viscosity levels of different samples. Rheograms may further include curves such as totalized torque – the area (integral) under the torque curve – defining at any moment of the test period the work which had been exerted on the sample.

The change from high to low shear conditions often has the additional benefit that the differences between similar samples are becoming even more apparent at low in comparison to high shear conditions. Fig. 149

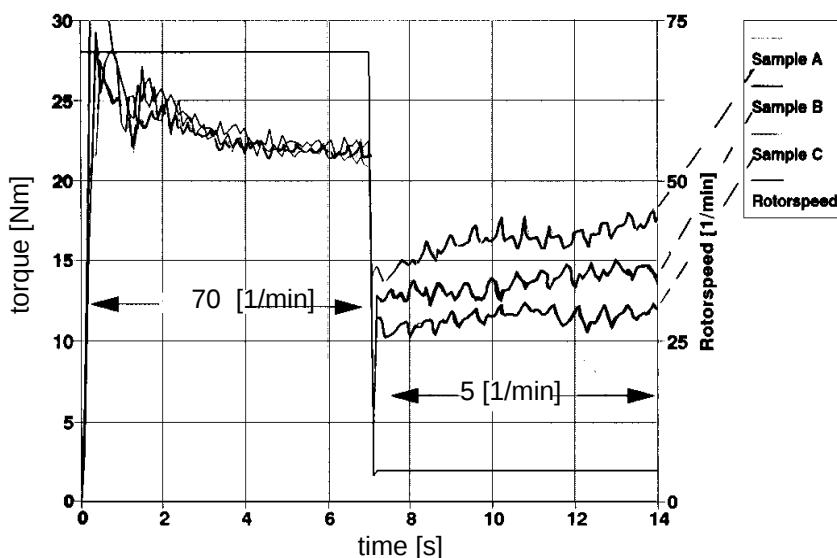


Fig. 149 Rheocord 90 : Mixer tests to differentiate rheologically between similar samples of natural rubber polymers

10.5 Testing processibility with mixer sensors

Absolute rheometry can only deal with more or less homogeneous solids and liquids within the limitations of laminar flow and linear visco-elastic responses. Torque rheometers with mixer sensors can look at samples not just as they are but how they can be processed in non-laminar, complex flow. How materials behave under complex process conditions is summarized under the term “processibility”. Interchangeable mixer sensors differing in size and rotor design can assess various aspects of this processibility on a relative basis for a very wide range of materials from polymers to food stuffs and to ceramic compounds. If one of these materials is passed through several stages of processing, each stage may present different problems of processibility and they may be looked at one after the other in separate tests. Whether a particular batch of a material can be made into a high quality product will then depend on the combination of its processibility in all production phases of which the melt viscosity may be one and often not the dominant factor.

Processibility problems can arise when:

- powders are tumbled or when gravity alone has to be sufficient to allow powders to flow uniformly through channels or hoppers.
- raw rubber polymers of very high molecular weight have to be masticated to allow further compounding.
- various types of polymers have to form a homogeneous blend.
- polymers such as PVC have to be melted and homogeneously mixed,
- liquids are metered to powders to see when they are balling-up to form dough-like masses,
- polymers have to be assessed for their combined shear and heat stability.

Mixers have been found to provide successful “down to earth-” or “pilot plant”-answers for these and other processibility problems which absolute rotational rheometers cannot deal with.

10.6 Examples of processability tests with mixer sensors.

10.6.1 Dry-blend powder flow.

PVC raw polymers are compounded with all the ingredients of a dry-blend formulation in a first production step making use of rapid speed mixers. The resulting powdery dry-blends can differ greatly with respect to their flow through channels such as an extruder hopper when just subjected to gravity. This flow will depend on parameters such as types of resin – their particle sizes, particle size distribution, porosity etc. – type of plasticizers and their viscosity at the test temperature, type and percentages of other compound ingredients such as fillers, stabilizers, lubricants etc. Some dry-blends flow easily through extruder hoppers while others perform such as “wet snow”, build stable bridges in hoppers and this then prevents a uniform filling of extruder screw flights even if the hopper seems sufficiently filled. A dry-blend that does not meet the first production stage requirement of good flow through a hopper is not processing well even if in a later production stage its melt viscosity is acceptable. It makes sense to design for special mixer sensors suitable for dry-blending in which plasticizers are added to the PVC powder during high speed, turbulent flow conditions at 100°C. Resulting rheograms are not only indicative of how and when the dry blend has absorbed the plasticizer sufficiently and becomes easy-flowing again but these curves are also informative of the PVC-particles, with respect to their particle sizes and their porosity.

10.6.2 Melting of a PVC dry-blend.

The second stage of polymer processing is the transformation of solid dry-blends or pellets to a uniform melt. This is usually realized along the major part of the extruder screw length. PVC-compounds which are difficult to melt can travel only partly fused up to the end of the screw. Since the degree of homogeneity of the melt does not change when the mass passes through the extruder head in a more or less laminar flow, such a non-homogeneously molten extrudate will be brittle and it will not perform well in applications. If the compound melts almost instantaneously in the feeding zone of the extruder screw the melt will be subjected to high shear and high temperature during the relative long time to reach the screw tip and it may already start to decompose unless it is well heat-stabilized.

It therefore makes sense again to devote a special test to define a sample's ability to melt under specified test conditions. It is not possible to actually define during the continuous extrusion process that point along the length of the extruder flight at which the mass is finally and completely molten.

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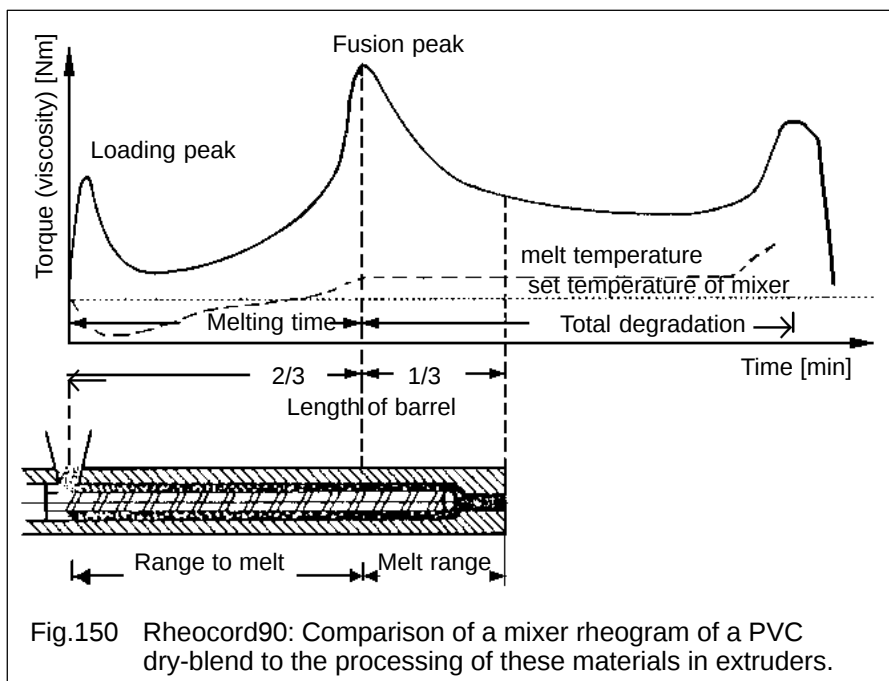


Fig.150 Rheocord90: Comparison of a mixer rheogram of a PVC dry-blend to the processing of these materials in extruders.

Instead a discontinuous test in a laboratory-size mixer is used for a comparative assessment of the rate of melting of a PVC-dry-blend: a specified volume of a cold dry-blend sample is forced in seconds into the mixing chamber controlled to some 150°C. Heated by the chamber walls and by the shear energy of the rotors the compound will start to melt which becomes apparent by an increase of the torque curve to a maximum. The process of the transformation from the cold powder to a melt can be monitored and plotted as a rheogram with respect to the test time. The time span between the filling peak to the melt peak defines a relative signal of the rate of melting – Fig. 150. Differences in the behavior of dry-blend samples to melt changes the length of the screw channel which is required for this process to reach the stage of a fully homogeneous melt. It has been shown that for a particular PVC-compound this screw channel length correlates to the time for the torque to reach the melt peak in a mixer rheogram. This test of melting PVC dry-blends grades new compounds on the background of proven compounds for a specific extruder and a specified set of production conditions such as extruder type, size and screw geometry, screw speed and set of extruder barrel temperatures. There are quite a number of compound parameters which may increase or decrease this property of melting PVC dry-blends: types of PVC

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related to their polymerization process, type and percentage of formulation ingredients such as heat and light stabilizers, lubricants, fillers, pigment, plasticizers etc. – Fig. 151

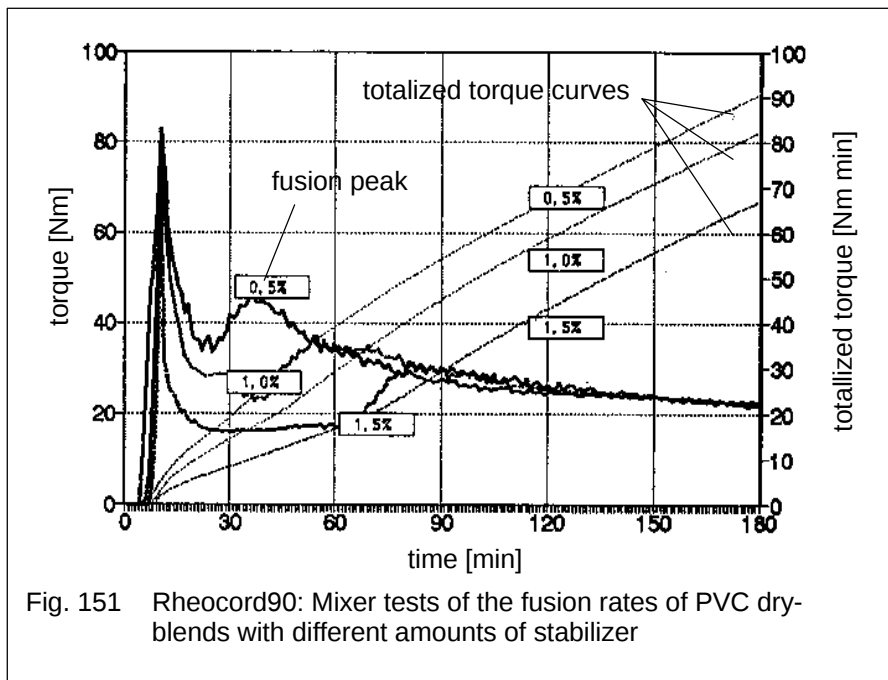


Fig. 151 Rheocord90: Mixer tests of the fusion rates of PVC dry-blends with different amounts of stabilizer

The relative nature of a test result classifying a compound as acceptable with respect to melting means that the same compound used in a larger extruder or with a totally different screw geometry may or may not perform well. This could mean that one would have to reformulate the compound if the process parameters such as the barrel temperatures or screw speed alone do not lead to an acceptable extrudate.

10.6.3 Testing the heat- and shear stability of polymers.

PVC degrades when subjected to a combination of high melt temperatures and/or high shear for an extended period of time. It changes chemically and physically: chlorine and hydrogen radicals freed from the polymer chain lead to chain scission and/or cross-linking of chain segments.

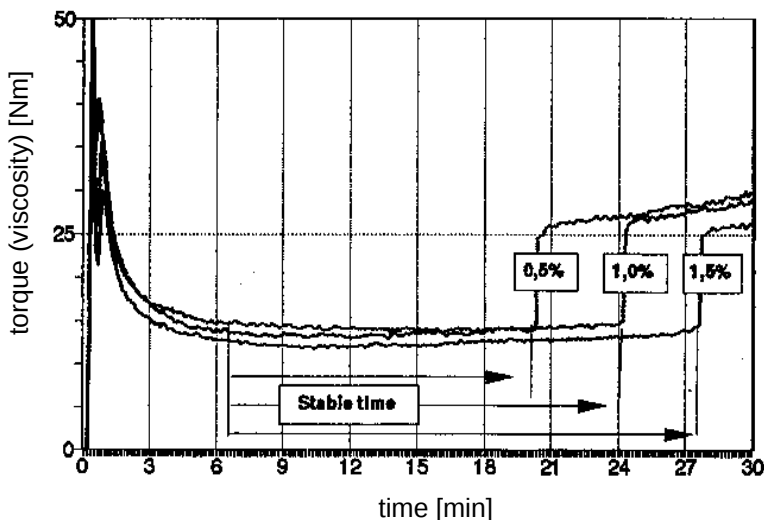


Fig. 152 Rheocord90: PVC Heat Stability Test on compounds containing different percentages of a particular lead stabilizer

These chemical changes result in additional physical changes which become apparent in rheograms with continuously decreasing curves. Alternatively the torque curve can start to suddenly rise which is an indication that in the final stage of degradation polymer cross-linking becomes dominant – Fig 152.

Degradation tests can also be performed on other polymer melts, which again either show some decrease of torque data with shear time or which as the result of cross-linking show a gradual increase of the torque curve. Covering the mixer entrance with a blanket of air, oxygen or inert gas adds an additional test parameter for these degradation tests. Alternatively volatiles which result from degradation can be removed from the mixing chamber for further chemical investigation to detect early phases of degradation.

10.6.4 Detecting shear sensitivity of raw rubber polymers.

Natural rubbers are of such a high molecular weight that they resist the incorporation of the other additives which form a rubber compound. Being natural products bales of “ribbed smoked sheet” are additionally very heterogeneous in their molecular structures within one bale and from bale to bale. To even-out these differences and to reduce the mean molecular weight it is a common procedure to masticate raw rubbers: In very large production

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mixers the polymers are subjected to high shear in order to mechanically break the molecular structures. This will reduce the viscosity and elasticity of the polymers so much that they will allow a uniform dispersion of i.e. large amounts of carbon blacks or other ingredients which are added only in small percentages such as sulfur, accelerators etc. The homogeneity of these ingredients is imperative for achieving high quality k rubber products such as car tires.

Mixers sensors can duplicate with some 60 grams of raw rubber polymers this process of mastication and determine how fast a polymer's torque/viscosity is reduced just thermo-mechanically alone or with the additional parameter of oxidizing chemicals such as Renazit 7, which greatly enhances the rate of mastication. In quality control one can either check the behavior of the raw rubber as it is supplied and how fast its viscosity can be reduced, or alternatively one can compare the effect of different chemicals supporting mastication on a standard polymer – Fig. 153.

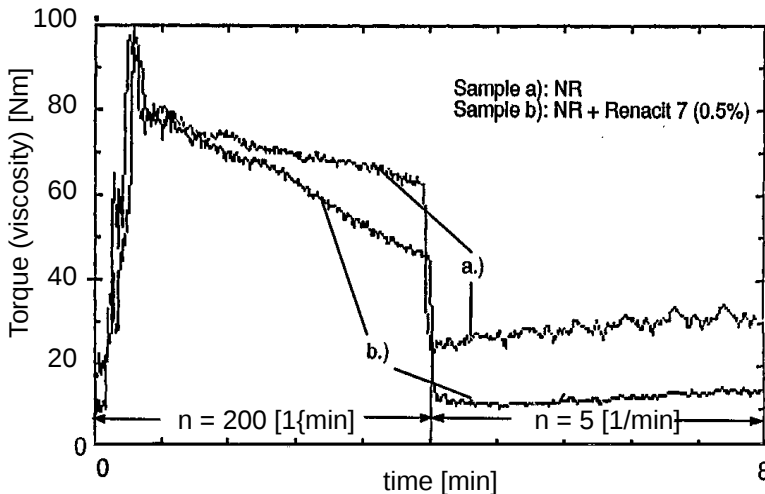


Fig. 153 Rheocord90: Mixer test of mastication of raw rubber polymers with and without Rhenacit 7 at 2 different rotor speeds.

10.6.5 Testing the oil absorption of carbon blacks

Carbon blacks are of utmost importance for the quality of rubber products and especially of car tires. Carbon blacks are graded in several aspects out of which the following two are very important: the free surface area of the primary carbon black particles given in units of square meters per gram – a value of $150 \text{ m}^2/\text{g}$ being not unusual – and the so-called “structure” of the carbon black defining the ability of this filler to adhere onto rubber molecules. Both characteristics of carbon black are difficult to determine. Mixing different batches of carbon blacks with rubbers which may be of unknown molecular structure will leave an uncertainty with respect to the carbon black performance. This leads to a revised test method: instead of testing the absorption of carbon blacks onto rubbers one determines the absorption of a low viscosity DBP-plasticizer – dibutylphthalat – in a batch of carbon black. DBP is an oily chemical which can be easily produced within tight specifications and it therefore provides the standard for the ability of the carbon black to absorb it.

Again a mixer test provides an automated test of carbon black batches. Special mixer sensors – e.g. of the Cabot design – are filled with a specified volume of the carbon black powder. While the rotors rotate tumbling this dry powder a burette is feeding the DBP into the mixing chamber at a rate of 4 ml/min . The normal time scale on the abscissa of the rheogram can be converted into a scale of the added DBP in units of ml/min . Depending on the type of carbon black and its structure, the mixed powder and oil suddenly will ball-up: they agglomerate to some high viscous dough resulting in a very sudden torque increase. – Fig. 154 a. A computerized evaluation of this rheogram will define the amount of DBP added before the torque curve reaches e.g. 70% of the peak torque and it is taken as a characteristic value that can be linked to the absorption of the filler into rubber compounds. Of course, one can also incorporate carbon black samples directly in polymers and determine what the relative effect the addition of a particular carbon black has on the torque/viscosity of the rubber compound – Fig. 154 b.

These tests are typical relative tests for the quality control of substances in which the change of composition is rheologically determined resulting in data only meaningful on the background of similar tests with standard carbon blacks. Especially the the DPB-absorption test which initially was probably quite empirical has proven its success in perhaps more than 100 000 tests worldwide for the differentiation of carbon black batches.

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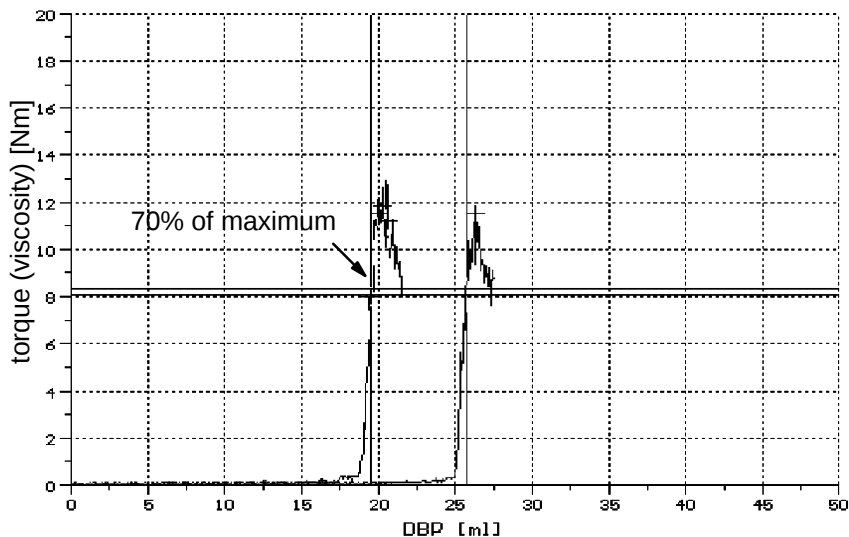


Fig. 154 a Rheocord90: Mixer tests of the DBP-absorption of two types of carbon black defined by the volume of DBP added to the carbon black powder to reach 70% of peak torque

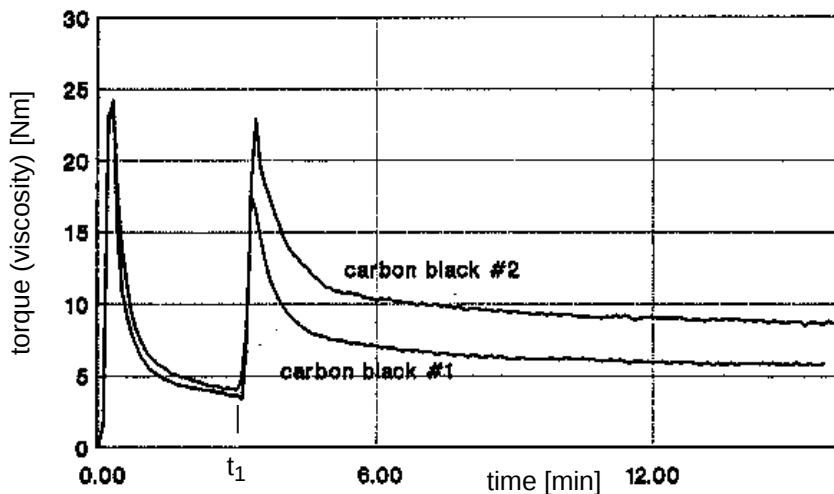
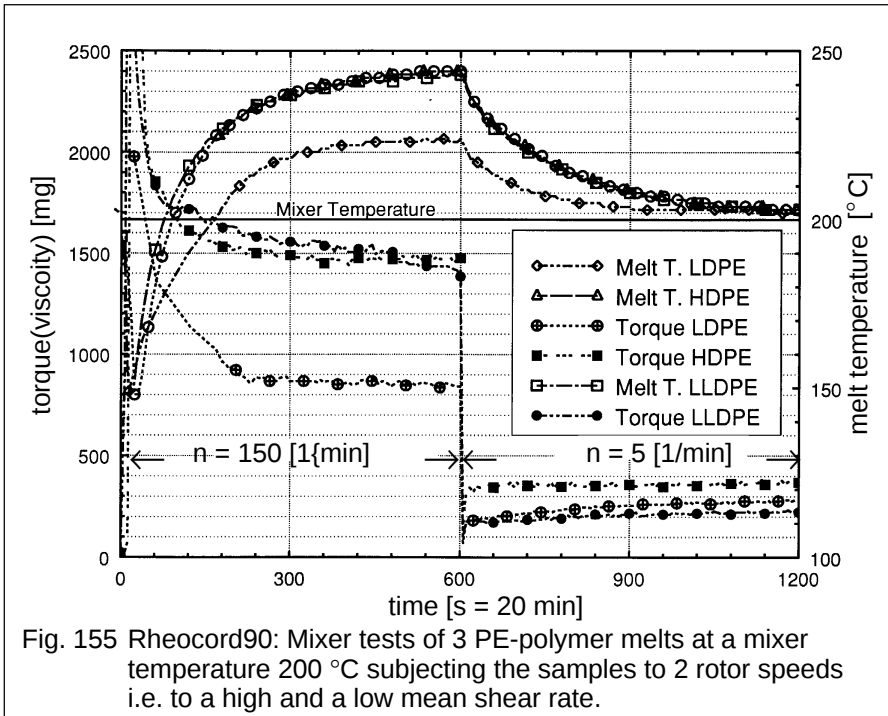


Fig.154 b Rheocord90: Mixer tests on a SAN polymer melt to show the differences when the above 2 types carbon black are incorporated at time t_1 .

10.6.6 Evaluation of molecular structure of polymers by mixer tests

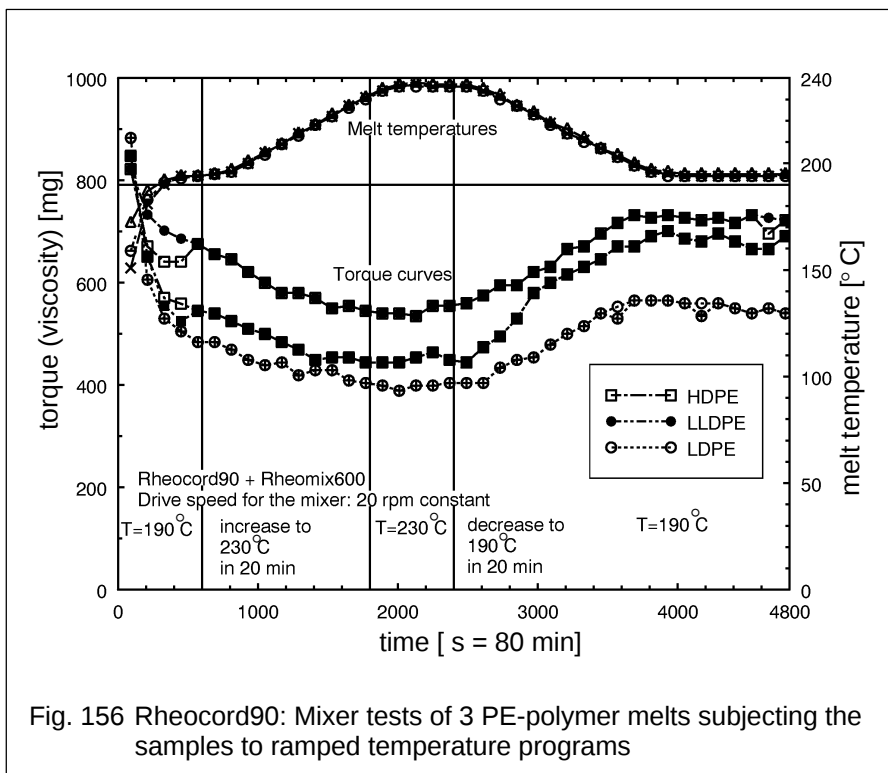


In the chapter “benefits of dynamic testing” – Fig. 76 – three types of polyethylenes were compared in a rotational rheometer. Mixer tests can give some comparable results for the differentiation of these polymers which differed in their mean molecular weight and the molecular weight distribution. At high rotor speeds/ high mean shear rates the LLDPE provides the highest resistance against being mixed while the torque curve of the LDPE is lowest. It is of interest to see that the LLDPE is more shear sensitive in comparison to the HDPE, because the two torque curves cross-over during the 10 min. high shear mixing period – this is something a dynamic or constant shear test in an absolute rheometer will not be able to show similarly.

During the low shear test phase the torque curves of the LLDPE and the LDPE change positions- this is in agreement with the combined viscosity curve of the capillary- and parallel-plate-rheometer tests shown in Fig. 80.

10.6.7 Determining the temperature dependence of viscosity.

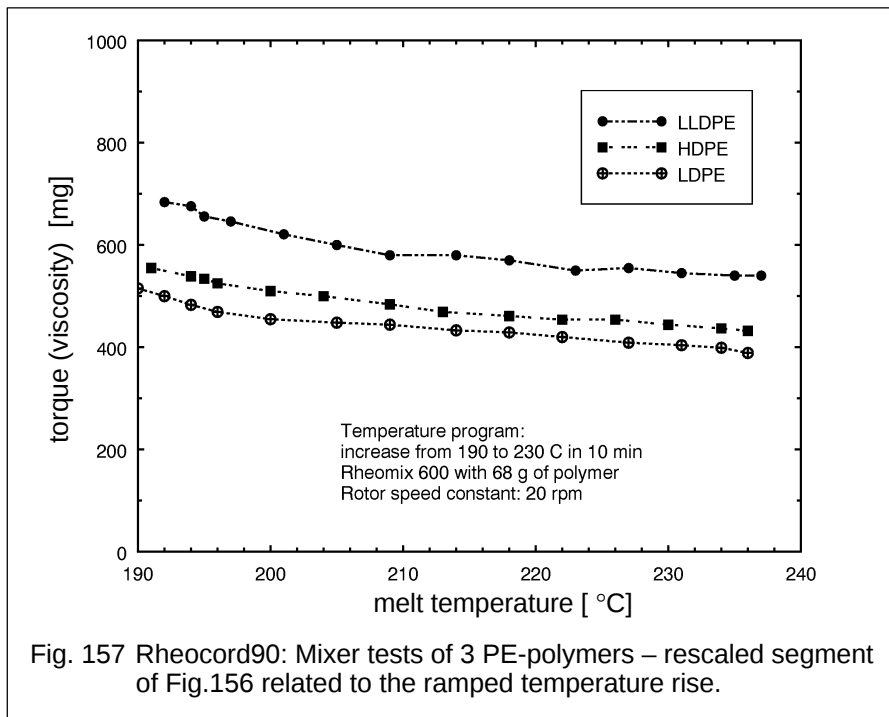
Mixer tests can be programmed so that the mixer temperature ramps linearly upwards or downwards (Fig. 156).



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Re-plotting the rheograms with torque as a function of temperature provides Fig. 157, which can be re-plotted with a logarithmic y-scale: this time the temperature is plotted on the abscissa in reciprocal degrees of Kelvin: Fig. 158



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The three polyethylene polymer melts are represented in Fig. 158 by 3 curves which are almost linear within the temperature range. Diagram of this type are known as an Arrhenius plots. Regression calculations on the three viscosity/temperature curves provide the coefficient for the Arrhenius equation: $\log \text{viscosity} = k_1 + k_2/T$ with T given in Kelvin.

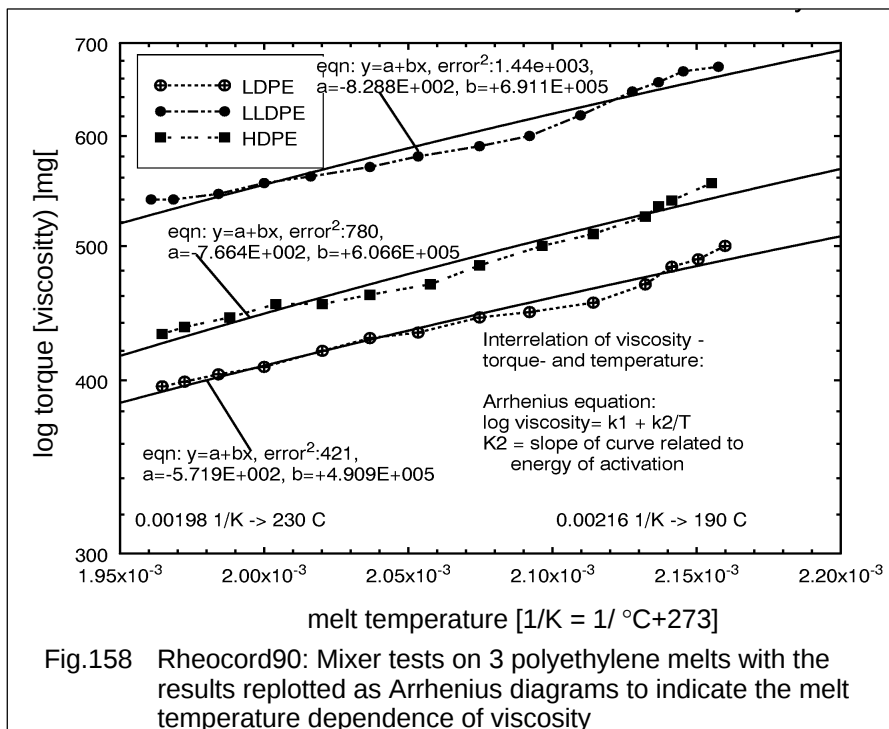


Fig.158 Rheocord90: Mixer tests on 3 polyethylene melts with the results replotted as Arrhenius diagrams to indicate the melt temperature dependence of viscosity

Arrhenius determined that the slopes of these plots are related to the energy of activation or the temperature dependence of the polymer melt. Knowing this correlation factor one may mathematically determine – under the assumption that the melt does not chemically nor physically degrade within a limited temperature range – how the viscosity of a polymer measured at a particular temperature would change at other temperatures.

It is hoped that the reader of this chapter on mixer rheometry with a limited number of examples of typical tests will see the potential of relative rheometry.

11. How to Select the Most Suitable Rheometer for a Given Sample?

A checklist worthwhile to use:

11.1 Knowing the basic behavior of the sample to be tested.

The first question to ask: Is the sample Newtonian or non-Newtonian?.

If you do not know, then a simple test in a viscometer/rheometer with variable shear rates will be indicative. If the resulting flow curve is a straight line, then the sample can be considered Newtonian.

Viscometer/rheometer alternatives are in this case:

- Gravity force viscometers such as Ubbelohde or Cannon-Fenske under the assumption that the viscosity of the liquid sample is not too high.
- Falling ball viscometer – with the same assumption as above.
- Rotational viscometer/rheometer providing one or several fixed rotor speeds. A sensor system with just a rotor suspended in a large open container will be sufficient rheologically – the actual test temperature must be measured and recorded.

If the flow curve of the sample is definitely non-linear within the specified shear rate range or if an initial step of the flow curve indicates a yield value, then the viscometer/rheometer choices reduce to:

- variable pressure capillary rheometers – preferably with a melt pump such as an extruder melting and homogenizing the sample continuously
- rotational viscometer/rheometer of either CS- or CR-design and either Searle or Couette sensor systems with narrow gap sizes.

If the samples are obviously not just viscous but show distinct elastic properties, and their yield values are technically important – the samples show a distinct solid behaviour – then the rheometer selection will reduce to:

- a sophisticated CS-rheometer with a low friction air-bearing for the rotor supported by a modern computer and a versatile software for a programmed testing and data evaluation.

11.2 Knowing the relevant shear rates for the processing or the application of the samples concerned.

This is a difficult question for many users of rheometers. This book has devoted a whole chapter to demonstrate how one can assess relevant shear rates. It has been pointed out that in many technical processes not just one but several often widely different shear rates are relevant. Most tests with rheometers combined with a particular choice of a sensor system or one type of a capillary will provide significant viscosity data only for one or two decades of shear rate. Asking for viscosity data covering 5 or more decades of shear rate is easy but the technical solution for this request will be high priced. This solution will often require not only several sensor systems but in some cases more than one type of rheometer. One will also have to consider that tests at very low shear rates to define, i.e. small yield values, provide significant data only if the chosen rheometer is sufficiently sensitive at a close to zero shear rate.

11.3 Do you want to measure absolute rheological data or do you want relative data which directly correlate to specific phases of production processes?

Absolute rheometer data provide a common basis for the comparison of data of different types of rheometers and their data can often be correlated to the molecular structure and/or the homogeneity of samples such as polymer melts.

On the other hand, often processability in its different forms has to be determined. Processability is a term that is only meaningful within the context of one company or department, because the data are compared to specific machinery or even segments of such a machinery. Their operators or supervisors must make the rheological data relevant for them and use deviations from standards for their quality control.

11.4 Special test requirements

Are there any special requirements such as:

- very high or low test temperatures,
- ambient or high pressures or vacuum,
- preparation changing porous, heterogeneous samples to compact, homogeneous and strain-released specimens
- blankets of air, of oxygen or inert gases. Many of these special requirements may be fulfilled at extra cost. With new requirements arising almost daily new technical solutions must be designed.

11.5 Budget restrictions

Of course, the available budget for the purchase of equipment will be the final decisive factor. Having thought of the preceding check points it is often more advisable to reduce some of the requirements – shear rate range, sensitivity, computer rating or scope of the software – than to buy a low price instrument. If possible choose rheometers which are designed in a modular way so that additional parts can be bought in years to come to upgrade the instrument for upcoming requirements.

“Bosses” should note: the most sophisticated rheometer is no good if there is not a qualified and motivated operator to sensibly choose proper test conditions and see to it that disturbances are avoided or at least are considered. But even this is not good enough because someone has to interpret the rheological results in terms of product quality, correlate data to molecular structure or make the data meaningful in terms of processability or establish that particular rheological value a customer will expect when buying the product.

In this context this book could be no more than a practical approach as an introduction of rheology and rheometry.

Thanks – The author gratefully acknowledges the support and advice given by the HAAKE rheology team and specifically by Dr. Hartmut Braun, David Holland, Wolfgang Marquardt and Jint Nijman.

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12. Literature References

The literature on rheology and viscometry is vast. In the following, only books or articles are mentioned which have been used for the writing of this book. Anyone interested in getting deeper into the subject of rheology and rheometry will find in the books mentioned large lists of specific literature. For further literature references please check the many international journals such as "Rheologica Acta" or "Journal of Rheology".

1. Viscoelastic properties of Polymers, 3rd edition, by John D. Ferry, John Wiley & Sons, Inc., New York, Chichester, Brisbane, Toronto, 1980
2. An introduction to rheology, by H. A. Barnes, J. F. Hutton and K. Walters, Rheology Series, 3, Elsevier Applied Science, London and New York, 1989
3. Praktische Rheologie der Kunststoffe und Elastomere, by W. Gleissle, H. M. Laun, M. Pahl, VDI-Gesellschaft Kunststofftechnik, Duesseldorf, 1990
4. Speed or stress-controlled rheometry?, by W. Gleissle, published in: Polymer rheology and processing, edited by A. A. Collyer and L. A. Utracki, Elsevier Applied Science, London and New York, 1990 – also presented at "Pacifichem 89", Honolulu 1989
5. Stresses in polymer melts at the beginning of flow instabilities (melt fracture) in cylindrical capillaries, by W. Gleissle, Rheologica Acta 21, 484 ... 487, 1982
6. Rheologie von Kunststoffschmelzen mit unterschiedlichem molekularem Aufbau, by H. M. Laun, Kautschuk+Gummi, Kunststoffe, 6.87., Dr. Alfred Hüthig Verlag, Heidelberg
7. Möglichkeiten und Grenzen der (Viskositäts-)Messung mit Rotationsviskosimetern, by Jint Nijman, lecture at the 102nd PTB-Seminar "Rotationsviskosimetrie newtonscher und nicht-newtonscher Flüssigkeiten – Metrologie, Normung, Qualitätssicherung" – October 1992, lecture at the seminar organized by the Physikalisch-Technische Bundesanstalt Braunschweig, published as a HAAKE-Germany publication, 1992
8. A general introduction to the theory of creep testing, by David Holland, published as a HAAKE-Germany publication, 1993
9. A general introduction to the theory of forced oscillation by David Holland, published as a HAAKE-Germany publication, 1993
10. Experimental errors when using rotational rheometers, by W. Marquardt and J. Nijman, Rheology 93, June 1993, Vincentz Verlag, Hannover,

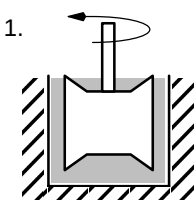
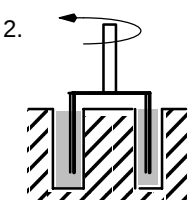
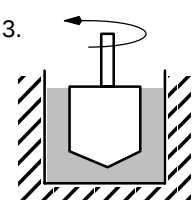
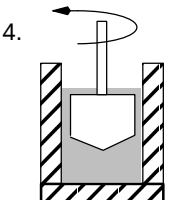
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Rheology

11. Introduction to normal stress, by J. Nijman, HAAKE-Germany publication, 1990
12. Die Rolle der Konsistenz bei Lebensmitteln, by B. Jacob, in Die Ernährungsindustrie, 3/94
14. Potential and limits for the rheological characterization of raw rubber polymers and their compounds, by G. Schramm, presented at a meeting of the Rubber Division of the American Chemical Society, Las Vegas, Nevada, USA, May 29 ... June 1, 1990, paper No.92
15. Testing the rheological characteristics of thermoplastic elastomers to provide guidelines for their application and their processibility, by G. Schramm, Kautschuk+Gummi, Kunststoffe, vol. 43 (1990), no. 12, pages 1074 ... 1082, Dr. Alfred Hüthig Verlag, Heidelberg
16. Rubber testing with the Defo-Elastometer, by G. Schramm, Kautschuk+Gummi, Kunststoffe, vol. 40 (1987), no. 8/87, Dr. Alfred Hüthig Verlag, Heidelberg
17. Comparison of several rheometers using 3 PE-polymers to link their results to molecular structure and processibility, by G. Schramm, HAAKE-Germany publication, 1993.
Also published in 2 parts as: Was sind relevante Schergeschwindigkeiten?, Kunststoffe 84 (1994), no. 2, pp151 ... 156, Karl Hansers Publishers Munich
and in the English edition as: What are the relevant shear rates for polymer processing?
2nd part as: Rheometrie gibt Auskunft über Struktur und Verarbeitbarkeit, Kunststoffe 84 (1984), no.6, June 1994
and in the English edition as: Rheometry provides information on molecular structures of polymers and their processibility.
18. Measuring blood viscosity with a rotational viscometer in line with the recommendation of the international committee for the standardization in haematology, by G. Schramm, HAAKE-Germany publication 1992.

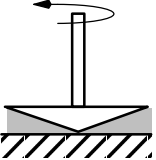
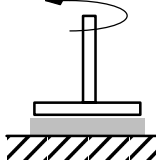
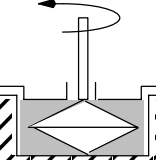
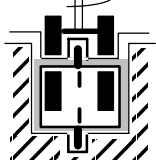
13. Appendix: Information on HAAKE Instruments

13.1 Comparison of rotational rheometers/viscometers

Type of instrument	Design features
A.Controlled Stress (CS) Rotational Rheometers Typical HAAKE model: RheoStress RS100 / 50: two almost universal CS rheometers which also features the alternative controlled rate (CR) and oscillation (OSC) test modes. Rotovisco RT10: a general purpose CR rheometer which also features the alternative controlled stress (CS) and oscillation (OSC) test modes. Optically both instruments look much the same and both use the identical sensor systems and temperature control units. The RT10 uses special roller bearings instead of air bearings (reduced low torque/stress capabilities – factor 100x – than the RS100) and a 60% higher torque range (allows the measurement of higher viscous fluids than the RS100). Schematic diagrams of typical interchangeable sensor systems (each available in several sizes) for the RS100/50 and RT10.	The RS100 applies in its controlled-stress-mode defined shear stresses to the test sample by means of an extremely low inertia, drag cup motor. The drive shaft of the RS100 is centered by an air bearing which ensures an almost frictionless transmission of the applied stress to the test fluid. The resulting deformation on the sample placed into a sensor system is detected with a digital encoder processing 1 million impulses per revolution. This resolution makes it possible to measure even the smallest yield values as well as extremely low strains or shear rates. The RS100 / RT10 can be computer-controlled to swap between both the CS and CR-modes and it can provide oscillating stress inputs and autostrain. A remote and manually controlled lift with variable lift speed axially positions a rotor versus a cup or a cone versus a plate. A thermal gap size compensation for any of the sensor systems is provided by a microprocessor-control. The sophisticated software with the “HAAKE windows” software controls both test routines and data evaluation.
1. Coaxial cylinders DIN 53018 for liquids of medium viscosity. 2. Coaxial cylinders – double gap – DIN 54453 for liquids of low viscosity.	3. Coaxial cylinders DIN 53019/ ISO 3219 for liquids of medium/high viscosity. 4. Coaxial cylinder sensor systems “high shear” for the measurement of liquids at high shear rates.
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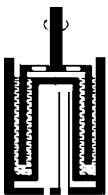
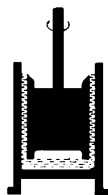
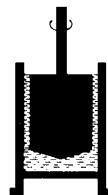
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Application	Limitations
The RS100 is an extremely sensitive and very versatile research instrument for rheologically complicated fluids being visco-elastic, non-Newtonian, showing yield points and shear-time effects on the rheological properties. More than 50 interchangeable sensor systems – coaxial cylinders-, cone-and-plate- and parallel-plate sensor systems as well as vane rotors allow the user to optimize test conditions for an unlimited number of samples from industries such as: cosmetics, pharmaceuticals, food stuffs, paints, coatings, adhesives, polymers, oils and even glass melts. Technical specifications: Angle resolution: $6 \cdot 10^{-6}$ [rad] Torque minimum: RS100 $0.2 \cdot 10^{-6}$ [Nm] Torque maximum: RS100 50 [mNm] RT10 80 [mNm] Rotor speed (CS) minimum: 10^{-7} [rpm] Rotor speed (CR) minimum: 10^{-1} [rpm] Rotor speed maximum: 500 [rpm] Sample size: 0.5 to 50 [cm³] Temp. range $\Rightarrow$ stand.: -50 to 350 [°C] optional -150/500 [°C] Oscillation $\Rightarrow$ frequency min: $2 \cdot 10^{-4}$ [Hz] dependent on sample: max: 60 [Hz]	The RS100 rheometer is designed to explore properties of solids and fluids of complicated rheological nature mainly with very low strains and at very low shear rates and with dynamic tests. These tests allow an insight into the molecular or “at-rest” structure of materials being both viscous and elastic. While providing a very high sensitivity to determine creep deformations at below-the-yield stresses, the RS100 cannot cope with tests of samples of high viscosity subjected to high shear conditions at the same time. Swapping to the CR-mode, the RS100 can successfully determine the thixotropy of samples by means of the hysteresis between the up- and down-ramp curves to match traditional test results. Testing low viscosity liquids, i.e. below 2 mPas, can lead to non-laminar flow – Taylor vortices and turbulence – causing serious errors for the viscosity measurement at higher rotor speeds. These very low viscous liquids which normally show an almost Newtonian flow property are often better measured by capillary- or falling ball viscometers.
5. Cone-and-plate sensor systems for the measurement of fluids of medium visco-elasticity. 6. Parallel-plate sensor systems for the measurement of fluids of high visco-elasticity.	7. Double cone sensor systems for the measurement of low viscous liquids. Influences of vapor loss and surface tension are minimized. 8. Sensor system for viscosity tests of liquids under pressure or vacuum.
5.  6. 	7.  8. 

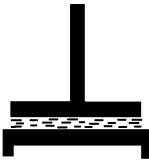
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Rheology

Type of instrument	Design features			
B1. Controlled rate (CR) rheometer Typical HAAKE model: Rotovisco RV30 combined with measuring drive systems M5 or M10 Former HAAKE models: Rotovisco RV1 / 2 / 3 Rotovisco RV100 / 12 / 20 Schematic diagrams of typical sensor systems (each with several models differing in their dimensions) which can be easily interchanged on Rotoviscos: Please note: the same sensor systems are used for Viscotesters:	The Rotovisco RV30 with a built-in RS232C serial port is designed to be operated with IBM-compatible computers. A sophisticated software package with the “HAAKE windows” format provides multiple choices for routine test programs and for data evaluation. Flow and viscosity curves are plotted or data is presented in tabulated form. The RV30 is a Searle-type rotational CR-rheometer. The DC drive is speed-controlled by a tachometer-generator. Variable rotor speeds/shear rates are preset and the resulting shear stresses are measured by means of interchangeable torque sensors: measuring heads for torque ranges 5 and 10 Ncm (50 – 100 mNm) The RV30 makes use of some 50 conventional interchangeable sensor systems which have ensured HAAKE a great degree of modularity for its rheometers for some 40 years to meet the rheological requirements of all kinds of fluids: coaxial cylinder, cone-and-plate, parallel-plate sensor systems and vane rotors.			
1. Coaxial cylinders “NV” with double gap – DIN 54453: for low viscous liquids 2. Coaxial cylinders “MV” DIN 53018: for medium viscous liquids 3. Coaxial cylinders “SV” DIN 53018: for liquids of high viscosity	4. Coaxial cylinders “MV DIN” – DIN 53019/ ISO 3219: for liquids of medium viscosity 5. Coaxial cylinders “High Shear HS”: for high shear testing of medium viscosity dispersions such as paints or adhesives			
1. 	2. 	3. 	4. 	5. 

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Rheology

Application	Limitations
The Rotovisco RV30 is equally suited for routine quality control and for research and development work. The modularity of the very many sensor systems offered provides this rheometer with its versatility with respect to the viscosity-, shear rate-, pressure- and temperature ranges. It may be used for the viscosity measurement of Newtonian liquids, but it really shows its technical potential when it is used to characterize non-Newtonian flow behaviour, yield values and thixotropy of an unlimited number of samples from industries such as: Cosmetics, pharmaceuticals, food stuffs, paints, coatings, adhesives, polymers, oils and even glass melts. Technical specifications: Rotor speed range: 10^{-2} to 10^3 [min⁻¹] Shear rate range: $4 \cdot 10^{-3}$ to $4 \cdot 10^4$ [s⁻¹] Shear Stress range: 0.2 to $7 \cdot 10^4$ [Pa] Viscosity: 5 to 10^9 [mPas] Sample size: 0.5 to 50 [cm³] Temp. range: -50 to 1700 [°C] Temperature control is either provided by direct electrical heating or by connection to external baths and circulators: -50 to 350°C. A special oven for testing glass melts provides temperatures up to 1700°C.	The RV30 does not provide information on the elastic properties of samples. For strongly visco-elastic samples the Weissenberg effect will limit running tests at high shear rates. This critical shear rate will be much lower than the maximum shear rate which could be used for the viscosity measurement of Newtonian liquids such as oils. Problems also arise when testing samples of high viscosity for some extended test period at high shear, because shear heating of the sample cannot be prevented even with an "ideal" temperature control. Testing low viscosity liquids, i.e. below 5 mPas, can lead to non-laminar flow - Taylor vortices and turbulence - causing serious errors for viscosity measurement. These very low viscous liquids which normally show almost Newtonian flow properties are better measured by capillary- or falling ball viscometers.
6. Cone-and-plate: for high shear testing	7. Parallel-plate: preferably for samples of high viscosity and with sizable yield values
6. 	7. 

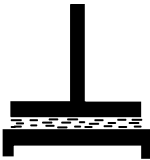
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Rheology

Type of instrument	Design features
B2. Controlled rate (CR) Rotational Viscometer Typical HAAKE model: Viscotester VT 550 Former HAAKE models: Viscotester VT 500/ VT501 which were optically similar but provided reduced technical specifications and Viscotester VT180/ VT24 <	

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Rheology

Application	Limitations
The VT 550 is primarily designed for routine QC-testing of both Newtonian and especially for non-Newtonian liquids of low up to high viscosity such as: cosmetics, pharmaceuticals, food stuffs, paints, coatings, adhesives, polymers and multi-grade oils. With an immersion sensor dipped into a liquid contained in any open container, the LED-display provides viscosity values in mPas or Pas units. With a Pt100 temperature sensor, the VT550 also measures the actual sample temperature. In the controlled deformation mode (CD) the VT550 monitors torque as a function of time to measure yield values using e.g. a vane rotor that is set to rotate at a very low constant speed in i.e. a yoghurt jar. The VT550 also measures thixotropy by means of the hysteresis between the up- and down ramp curves allowing sufficient time at the upper shear rate level to fully reach the sol state. Technical specifications: 10 sets of 10 fixed rotors each within max/min speeds: 800 / 0.5 [rpm] Shear rate: 0.6 to 32000 [1/s] Shear stress: 1 to 10^5 [Pa] Viscosity: 1 to 10^9 [mPas] Torque ranges: 0.5 to 400 rpm: 0.01 to 3 [Ncm] speeds 400 to 500 limited to 2 [Ncm] Sample size: 0.5 to 50 [cm³] Temperature: -50 to 250 [°C]	Testing samples of a viscosity of lower than 3 mPas using maximum rotor speeds can result that the viscosity measurement may be disturbed by Taylor vortices and turbulence: this may lead to very erroneous viscosity results. The Viscotester VT550 does not provide information on the elastic properties of samples. Flow and viscosity curves in one test run are pointed with a maximum of 10 test points but the computer can combine the 10 sets of 10 fixed rotors speeds to plot both flow- and viscosity curves with 100 measuring points. This is almost as good as the continuous curves which may be provided by Rotoviscos.
6. Cone-and-plate: for high shear testing	7. Parallel-plate: samples showing high yield values
6. 	7. 

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Rheology

13.2 Tabulated comparison of capillary viscometers

13.2.1 Absolute viscosity data

Type of instrument	Design features
C1. Variable pressure capillary viscometers provided with rheological dies. Typical HAAKE Model: Torque rheometer e.g. Rheocord – models “90” and “9000” – with an attached RHEOMEX (either single screw or twin screw extruder sensor) and a rheological rod- or slit die.	Rheological rod dies: Diameters D : 1 to 2 mm Length L: 10 to 40·D The pressure loss $\Delta P \approx$ shear stress τ along the rod capillary is measured as the pressure difference between the pressure in the entrance region and the ambient pressure at the exit. The flow rate $Q \approx$ shear rate is predetermined by a melt pump or it is weighted per time unit as the extrudate weight. Rheological slit dies: Width: Wide, at least 10 mm Depth: Small, i.e. 1 to 2 mm Length: Very long, i.e. at least 40 to 100 mm between the pressure sensors. The pressure loss ΔP is measured between two points/ports in the capillary spaced sufficiently apart from both the entrance and the exit to eliminate entrance effects. Normally the rheological dies are attached to laboratory-size extruders which melt and homogenize the polymers within a short time span. These extruders supply the pressure to feed the melts at variable extrusion rates through the capillary continuously.
C2. Gravity force capillary viscometer. Typical Models: Ubbelohde and Cannon-Fenske.	Capillary diameter D: 0.5 to 5 mm length L: defined as multiples of D L/D-ratios should be better than 50:1 to keep the influence of entrance and exit effects on test results small. The kinematic viscosity is measured by determining the time span Δt at a defined volume of this liquid requires to pass through the capillary. This time value Δt can be measured by means of either a stop watch or automatically by means of light beam sensors monitoring the drop of the liquid level between two graduation lines along the capillary.

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Application	Limitations
A wide range of defined shear stresses and shear rates can be covered. Suitable for the rheological testing of both Newtonian and non-Newtonian liquids, i.e. mostly polymer melts. Absolute viscosity values are provided. The test procedure can be fully automated to cover a predetermined shear rate range. The measured data is stored and may be evaluated to provide diagrams of flow- and viscosity curves rheologically defining the flow behavior and the molecular structure of the tested polymer melt. Technical specifications: Viscosity range: $\eta = 10^2 - 10^6$ [Pa · s] Shear rate range: $\dot{\gamma} = 10 - 10^4$ [1/s] Sample size: 500 to 1000 grams The die swell of the rod die extrudate having left the capillary provides a relative signal which is proportional to the shear rate dependent elasticity of the melt. Increasing shear rates beyond a critical level $\dot{\gamma}_{crit}$ when testing visco-elastic melts may lead to melt fracture – rough extrudate surface. Operators must determine $\dot{\gamma}_{crit}$ and must choose test conditions which do not surpass this shear rate.	Not well suited for very low viscous liquids. Does not allow measurement of yield points and thixotropic structures. Signals of shear stress τ and of flow rate Q measured at low shear rates are often very insignificant leading to viscosity data which could be almost meaningless. Capillary viscometry as such provides just viscosity and no elasticity data. Elasticity data of die swell measurements have only a relative character especially since the melt is checked for its die swell only seconds after having left the die exit and thus the melt does not have time enough to fully retard. Pressure sensors installed in rheometer dies have to be selected to meet the maximum absolute pressure to be expected in the capillary. Pressure differences often encountered in quality control tests of similar melt samples can be within the limits of the tolerance level of those pressure transducers, thus making a clear differentiation between those samples difficult. Corrections such as “Weissenberg/Rabinowitsch” and “Bagley” are required if capillary viscometer data of a particular sample is to be compared with those of other rheometers.
Suitable for Newtonian liquids only. Technical specifications: Viscosity range: $\eta = 0.5$ to 10^4 [mPa·s] Sample volume: 5 - 20 [cm³] Temperature range: up to 150 [°C] Delivers absolute data of kinematic viscosity with a very high level of accuracy. To convert these data to the corresponding dynamic viscosity requires the knowledge of the density ρ of the liquid at the test temperature.	Shear rates decrease non-linearly from the capillary wall towards the capillary center when non-Newtonian liquids pass through the capillary. With the liquid level dropping within the test period, this in effect results in time-dependent shear stress values. With shear rates not exactly defined across the capillary shear rates and shear stresses varying with time, the gravity force capillary viscometers are therefore not suitable for non-Newtonian liquids and especially those showing a thixotropic structure or those characterized by a yield value.

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Rheology

13.2.2 Relative viscosity data

Type of instrument	Design features
C3. Melt indexers As specified by ASTM, BS, DIN, or other national standards for the measurements of polymer melts.	The melt indexer consists of a vertically positioned, heated barrel and a plunger which is tightly fitted into the barrel. The barrel can be fitted with nozzles of variable dimensions. An internationally standardized nozzle has the the following dimensions: Capillary length: $L = 8 \text{ mm}$ Capillary diameter: $D = 2.095 \text{ mm}$ $L/D \approx 4$ The normally pelletized polymer sample is poured cold into the heated barrel where it melts being subjected to the heat conduction from the outside. Dead weights on the plunger and the test temperatures can be varied. The “melt flow index” (MFI) defines the amount of extrudate given in units of grams which is extruded within a period of 10 minutes with a specific weight and a given test temperature being the test parameters.
C4. Orifice viscometers Typical Models: Ford or DIN-cups. Engler and Saybolt-Redwood.	It consists of a wide cup-type reservoir and a “capillary” shrunk to a simple hole or L/D ratios of less than 10/1. By means of a stop watch the time is measured for a defined liquid volume filling the cup up to the upper rim to flow through the “capillary”. Engler Orifice Viscometer: The outflow time of any liquid sample is compared to the outflow time of water.

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Rheology

Application	Limitations
Relative classification of polymers which easily transform to a homogeneous melt without a significant percentage of air enclosures. These polymers must be sufficiently heat-resistant against a polymer degradation during a melting period of some 10 minutes resulting in either a viscosity decrease or viscosity increase – cross-linking. Technical specifications: Sample size [g]: 20 - 100 Temperature range [°C]: up to 350 Dead weights [N]: 3.25 , 21.6, 50, 216	High entrance and exit effects strongly influence the measured relative viscosity data. It would not make sense to try “corrections” in order to transform the test results to absolute viscosity data. Shear stresses and shear rates – often in the magnitude of 1 (1/s) – encountered in a melt indexer are very much on the low side compared to those typical for production machines. Test results therefore often describe the processing properties of polymer melts related to such a processing incorrectly. The usage of melt indexers is today limited mainly to the testing of polyolefines melts.
Relative classification of Newtonian liquids. Transformation of test results into absolute viscosity values in units of “mPa·s” is not possible. Technical specifications: Sample size: 50 - 100 [cm³] Means to provide a defined test temperature are not provided. When testing at room temperature this temperature value must be additionally noted. Measured outflow data of a particular fluid can be corrected for variable room temperatures when outflow versus temperature tables are available.	Viscosity related “entrance effects” are measured rather than real viscosity data. Unsuitable for non-Newtonian liquids especially those with a yield point and those showing a thixotropic structure. Orifice viscometers today are of solely historical interest in the commercial and technical world. They are neither suited for the viscosity measurement of Newtonian nor of non-Newtonian liquids. Just being cheap is not a sufficient argument for technically important questions.

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Rheology

13.3 Comparison of the falling ball viscometer and the drawn-ball viscometer

Type of instrument	Design features
D1. Falling Ball Viscometer Typical HAAKE Models: a) Hoepppler Falling Ball Viscometer It corresponds to the DIN 53 015 standard. b) Micro-Falling Ball Viscometer ("Microviscometer")	The viscosity of a fluid is measured by means of the falling-time of a ball rolling through a sample contained in a tube. This viscometer can be adapted to samples of a varying viscosity by changing the diameter of the balls and/or their specific weights. The Microviscometer is a special version of the falling ball viscometer: it uses medical syringes for liquid samples of less than 0.5 cm³ and gold-plated steel balls which can be automatically lifted by a rotating magnet in cycles of 15 sec. An unlimited number of cycles can be run for a particular sample until constant fall-times indicate constant test parameters such as the temperature of the sample.
D2. Drawn-Ball Viscometer Typical HAAKE Model: Viscobalance	This instrument uses a balance beam. On its right side varying weights may be placed. On the other side a ball-rod – a thin rod with an attached ball – is attached, which is submerged on its ball-side in a sample of high viscosity contained in a tube. This tube can be jacketed for temperature control by means of liquid baths and circulators reaching up to 300°C. Placing weights on one side of the balance beam will pull the ball-rod upwards through the sample to be tested. The timed speed of the ball-rod moving upwards and the weight trays downwards for a given weight block can be converted to a viscosity-related signal.

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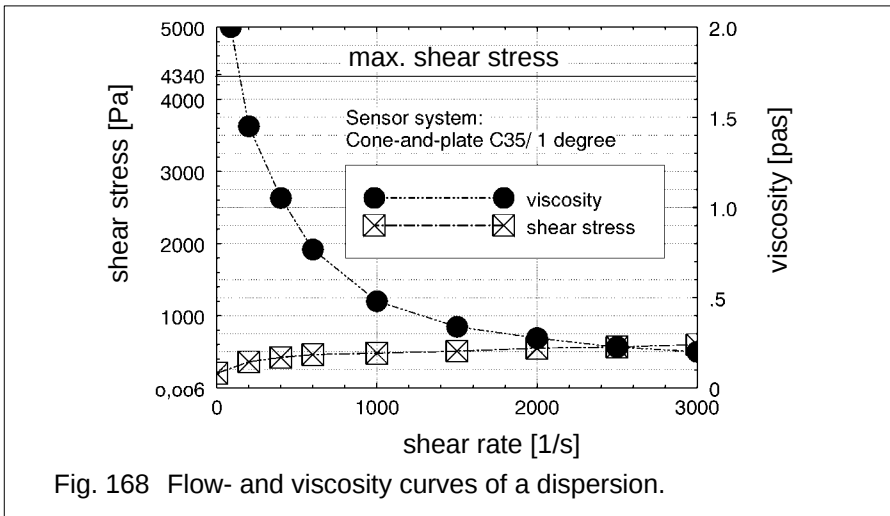
Rheology

Application	Limitations
Measures the viscosity of low to medium viscous, transparent Newtonian liquids accurately. Technical specifications: Viscosity range: $\eta = 0.5$ to 10^5 [mPas] Sample sizes: Hoeppler falling ball viscometer: some 100 [cm³] (acc. to ball size) Microviscometer: 0.3 or 0.5 [cm³] Temperature range: 5 to 60 [°C] Liquid temperature control with bath and circulator	Must not be used for liquids other than Newtonian liquids. Unsuitable for non-transparent liquids and for those of high viscosity.
Suitable for Newtonian liquids even when they are non-transparent and of high viscosity such as oils, bitumen or tars. Technical Specifications: Viscosity range: $\eta = 0.5$ to 10^5 [mPas] Temperature range: -20 to 120 [°C] Model VWB 301: up to 300 [°C] This special, high temperature model of the Viscobalance is DIN-standardized for the viscosity testing of bitumens Sample size: some 100 [cm³]	The Viscobalance must not be used for non-Newtonian liquids if more than relative viscosity data is required. Tests including the cleaning process are troublesome and often quite time-consuming. The Viscobalance today is most likely exchanged for modern rotational rheometers with cone-and-plate sensor systems, which require less of a sample, heat faster to the test temperature and provide information on non-Newtonian flow properties of samples such as bitumen blended with polymers.

13.4 An example of a stepwise variation of test conditions for a rotational rheometer to improve the relevance and accuracy of data

For the rheological testing of an unknown sample even experienced operators must choose a more or less arbitrary rheometer setup for a first test run: a particular rheometer, a particular sensor system, a reasonable shear rate range and a suitable test temperature. The results of this first test are then used to improve the parameters for further tests.

The result of such an initial test in the form of a flow- and viscosity curve may be:



The operator must now consider in which direction the test conditions should be improved:

- Going to even higher shear rates: this may provide information on samples which may strongly shear-thin at higher shear rates encountered in coating processes.
- one may be especially interested in the yield value of the sample to ensure that solid particles in dispersions are prevented from sedimenting. Such a test target requires very low shear rates and a sufficiently sensitive shear stress range to keep the “noise”-level of such a measurement low.

Assuming that an operator has all types of HAAKE rheometers/viscometers at his disposal, it may be useful to look at the basic torque range differences of these instruments.

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	VT550	RV30	RT10	RS100
Test modes	CR-CD	CR	CR-CS	CS-CR
Rotor speeds:				
max/min [rpm]	800 / 0.5	1000 / 0.01	1000 / 0.1	500 / 0.0001
speed ratios	16 000 :1	100 000:1	10000:1	5 000 000:1
tau max/min [mNm]	30 / 0.01	100 / 0.1	80 / 0.01	50 / 0.00005
ratio max/min	3000:1	1000:1	8000:1	1 000 000:1
Temperature ranges [°C] for particular sensor systems:				
immersion sensor systems				
no temp. control	5/95	5/95	–	–
circulator temperature control:				
for cone-and-plate:	–30/200	–30/200	–50/350	–50/350
for coaxial cylinder:	–30/100	–30/100	–50/200	–50/200
direct electrical heating:				
high temperature:	–	–	–150/500	–150/500

First conclusions from this table:

1. The Viscotester has the smallest and the RheoStress RS100 the largest rotor speed ratio. These ratios correlate to the shear rate ranges which these viscometers/rheometers are capable of handling.
2. The Rotovisco RV30 has the smallest and the RheoStress RS100 the largest shear stress ratio, but the RV30 provides the highest maximum torque.
3. Thermal liquid baths and circulators with refrigeration allow testing down to –150°C and up to 350°C. Testing at very high temperatures up to 500°C requires special electrically-heated attachments available only on the Rotovisco RT10 and RheoStress RS100.

Apart from the basic speed and torque ranges, the various rotational rheometers/viscometers provide, operators can choose the most suitable of the sensor systems among those available. They are rheologically defined by their shear stress factor “A” and their shear rate factor “M”. The relevant shear stress ranges an operator will choose are defined **by the combination** of the specifications related to the rheometer and the particular sensor system.

$$\tau_{\min/\max} = M d_{\min/\max} \cdot A$$

$$\dot{\gamma}_{\min/\max} = \Omega_{\min/\max} \cdot M$$

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Rheology

The example of a rheometer RheoStress RS100 combined with 3 coaxial sensor systems is given to show the influence of the factors A and M on the resulting shear stress- and shear rate ranges. These factors are given in the instruction manual of the rheometer concerned which lists all sensor systems available. They may not be named A and M by other rheometer manufacturers:

Sensor Systems		rotor diameter	A	M
		D_i [mm]	[Pa/Nm]	$[s^{-1}/rad\ s^{-1}]$
Coaxial Cylinder	Z10DIN	10	385800	12.29
	Z20DIN	20	48230	12.29
	Z40DIN	40	6030	12.29
Double-gap cylind. DG 40:		$D_a = 40$	3997	13.33
Cone-and-plate	C20/1°	20	477500	57.3
	C35/1°	35	890900	57.3
	C60/1°	60	17680	57.3
	C20/4°	20	477500	14.32
	C35/4°	35	9090	14.32
	C35/4°	60	17680	14.32
"High shear" coax. cyl. HS25		10.075	88090	440.5

The gap size for the Z40DIN is 1.7 mm; for the HS the gap size is 25/1000 mm. The larger the factors A and M are, the wider are the shear stress- and the shear rate ranges. The exchange just of the above sensor systems allows the user to shift the shear rate range by a factor of about 35 and the shear stress by a factor of about 120. This provides the versatility required to cope with the viscosity measurements of fluids as different as blood and plasma, yoghurt, melt adhesives or even bitumen at lower temperatures. Considering the shear rate range covering 10 decades which might be required – see chapter on "relevant shear rates" – this rheometer with all its sensor systems can still cover only a segment of the scope of testing research may require.

The limits of the RheoStress RS100 range of torque M_d are:

$$M_{d\ min} = 1 \quad \mu Nm = 10^{-6} \text{ Nm}$$

$$\text{option} = 0.2 \cdot 10^{-6} \text{ Nm}$$

$$M_{d\ max} = 5 \times 10^5 \mu Nm = 0.05 \text{ Nm}$$

The limits of the RS100 rotor speeds are:

$$N_{\min} = 10^{-2} \text{ min}^{-1} \Rightarrow \Omega_{\max} = 2 \cdot \pi \cdot 10^{-2}/60 = 0.01047 \text{ rad/s}$$

$$N_{\max} = 500 \text{ min}^{-1} \Rightarrow \Omega_{\max} = 2 \cdot \pi \cdot 500/60 = 52.36 \text{ rad/s}$$

Theoretically the minimal rotor speed could be even $n_{\min} = 10^{-4} \text{ min}^{-1}$ which equals one full revolution of the rotor in almost 7 days, but this represents ob-

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viously a very impractical test condition. The initial test of a dispersion resulted in Fig. 168. The RS100 allowed at maximum rotor speed the cone-and-plate sensor system C35/1° to reach a maximum shear rate of $\dot{\gamma} = 3000$ 1/s. The sample was obviously characterized by a yield value, but in Fig. 168 this yield value represents only 5% of the full shear stress range.

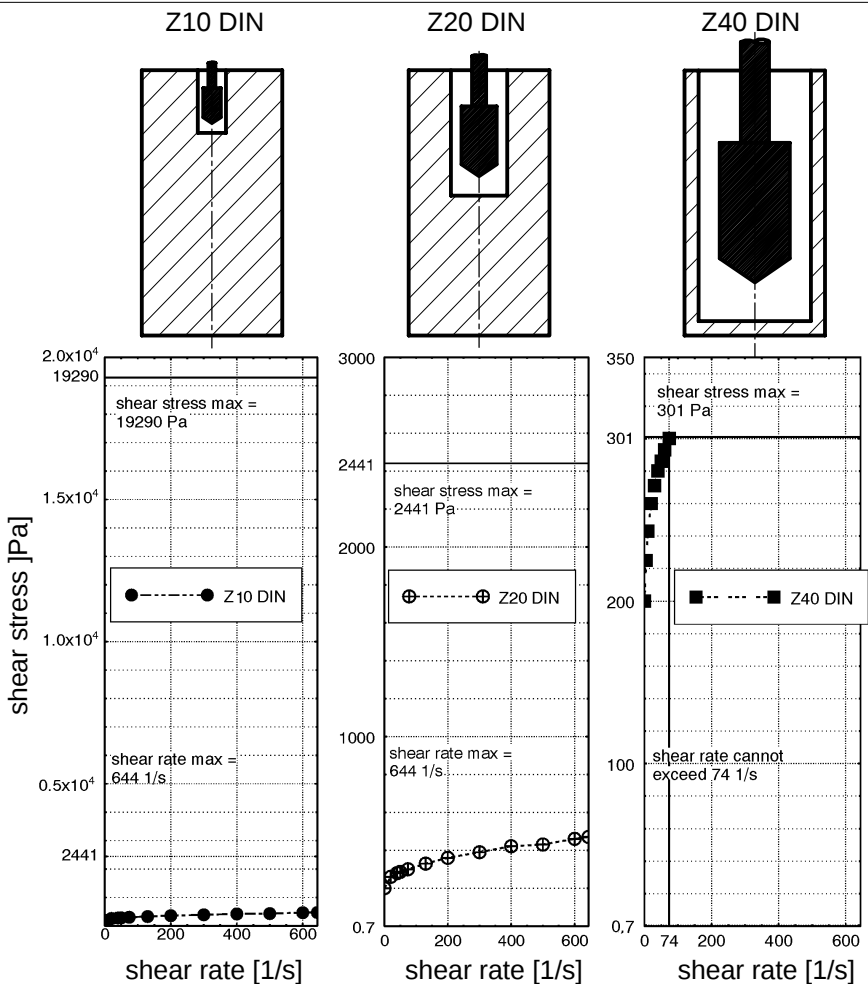


Fig.169 Comparison of flow curves of 3 geometrically similar sensor systems

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Fig. 169 is used to show the effect of 3 coaxial cylinder sensor systems Z10 DIN, Z20 DIN and Z40 DIN which are of the DIN/ISO design and are similar in shape but different in their rotor diameter D_i . Still their ratios of R_a/R_i and their factors M are identical which means that they provide the same shear rate ranges. The Z40 DIN is the largest of the 3 sensor systems and this results in the smallest factor A and the narrowest, most sensitive shear stress range $\tau = 0$ to 301 Pa. This shear stress value represents only 1.6% of the shear stress range of the Z10 DIN.

The ranges of shear stress and shear rate for these sensor systems are:

	Z10 DIN	Z20 DIN	Z40 DIN
$\tau_{\min}$ [Pa]	0.39	0.048	0.006
$\tau_{\max}$ [Pa]	$19.3 \cdot 10^3$	$2.4 \cdot 10^3$	$3.1 \cdot 10^2$
$\dot{\gamma}_{\min}$ [1/s]	0.01	0.01	0.01
$\dot{\gamma}_{\max}$ [1/s]	644	644	644
$\eta_{\min}$ [Pa·s]	30	3.8	0.47
$\eta_{\max}$ [Pa·s]	$1.9 \cdot 10^6$	$2.44 \cdot 10^5$	$3.01 \cdot 10^3$

Fig. 169 indicates that using the Z40 DIN means that for the dispersion tested, the full range of shear stress is already reached at a shear rate of $\dot{\gamma} = 74$ 1/s. While the yield value $\tau_0 = 200$ Pa is 2/3 of the Z 40 DIN shear stress range, the shear rate range is limited by the upper shear stress value. With the Z20 DIN one can reach the maximum shear rate this sensor system offers for the sample used for this comparison, but now the yield value is only about 10% of the shear stress range of this sensor system. When trying to optimize the yield value measurement, the shear stress range of the Z10 DIN is then even more unfavorable for this sample of a dispersion. If the operator would aim at extremely high shear rates he could choose instead of the Z40 DIN the “high shear HS” sensor system which can raise the maximum shear rate to more than 20000 1/s.

Fig. 169 indicates how the different sensor systems result in flow curves of variable shapes and as a consequence variable significance levels. The operator having considered the rheological requirements for the data interpretation with respect to a sample's behavior in processing or usage must then choose the most suitable of the sensor systems available with respect to the shear rate and shear stress ranges. It is important that quite a number of sensor systems are at disposal to choose the best sensor systems for a wide family of samples subjected in their processing to wide ranges of shear rates and test temperatures. Additionally further considerations must be included such as particle sizes, problems caused by rapid or slow breakdown or recovery of thixotropic structures, sedimentation of particles or shear heating. Choosing sensor systems will always require an optimum compromise.

This example of test parameter variations has dealt with viscosity measurements only. For the rheological characterization of visco-elastic samples which requires the combination of viscous and elastic data, one has to improve test conditions likewise in steps. While one should stay as long as possible within the framework of linear visco-elasticity and choose sensor systems and shear rates accordingly, one has to keep in mind that most production processes may reach beyond the limits of linear visco-elasticity. It is then worthwhile to choose test parameters to go beyond those limits to improve the correlation of the rheological data with the real-life performance of fluids.

13.5 Examples of typical genuine rheograms of an RS100 in the CS-mode

Two types of printing inks were tested with a RheoStress RS100 making use of a parallel-plate sensor system with a plate radius of 10 mm and a gap size between the plates of 2 mm. The test temperature was 40°C.

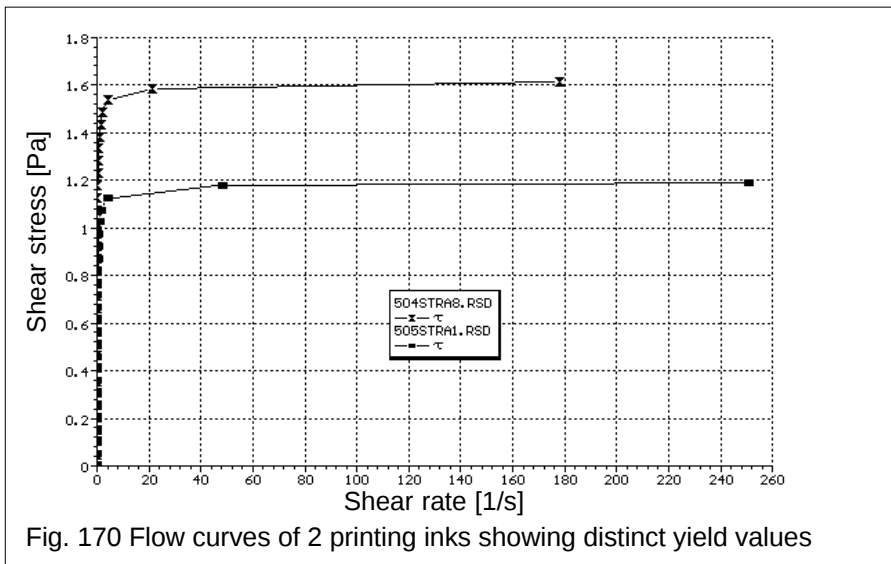


Fig.170: the flow curves indicate that the ink 504 provides a higher yield value in comparison to ink 505. Once the yield value is surpassed, the rotor starts to rotate. Being highly thixotropic the viscosity of these inks decreases fast and this allows the rotor to accelerate even without any greater increase of shear stress to reach almost instantaneously the maximum rotor speed of 500 min⁻¹.

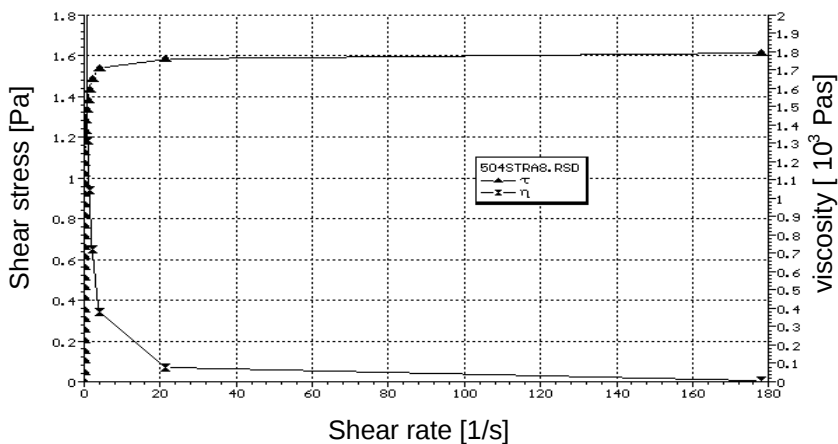


Fig. 171 Flow- and viscosity curves of the 504 printing ink

Fig. 171: The flow curve of the ink 504 in Fig. 170 is augmented by its viscosity curve. The viscosity of this ink just above the yield stress is close to infinity, but it then drops many decades in magnitude with the shear rate increasing to 180 1/s.

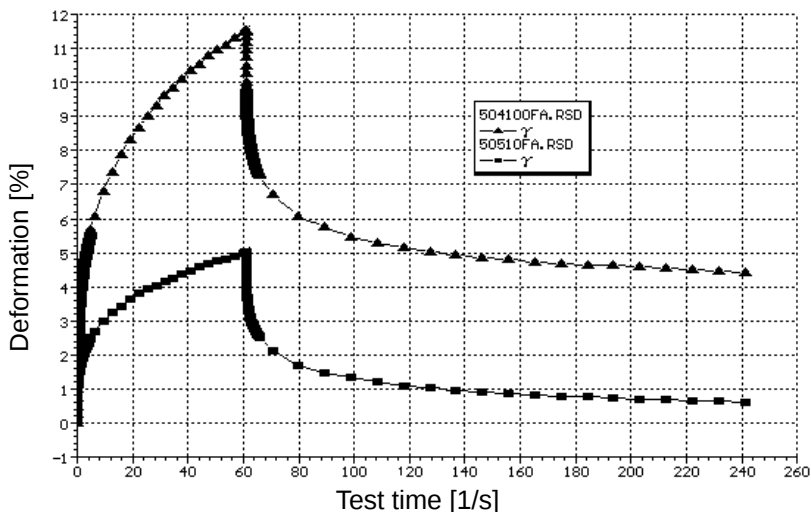


Fig. 172 Creep and recovery curves of the two printing inks

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The creep and recovery tests of these printing inks show a similar difference between the ink samples as the flow curves of Fig.170. The curves are plotted as deformation versus shear time. For a preset constant shear stress value of $\tau = 100$ Pa, the lower viscous ink sample 505 deforms more than the ink 504 during the creep phase. In the early phases of both creep and recovery the software is designed to collect 10 times more data per time unit than in the later phases which allows the user to look in more detail at the deformation when it changes most rapidly. This is demonstrated in Fig.173.

During the recovery phase of 3 minutes the ink 505 recovers some 60% of the creep deformation while the ink 504 recovers almost 90%. This indicates that the ink 504 is more elastic than the ink 505.

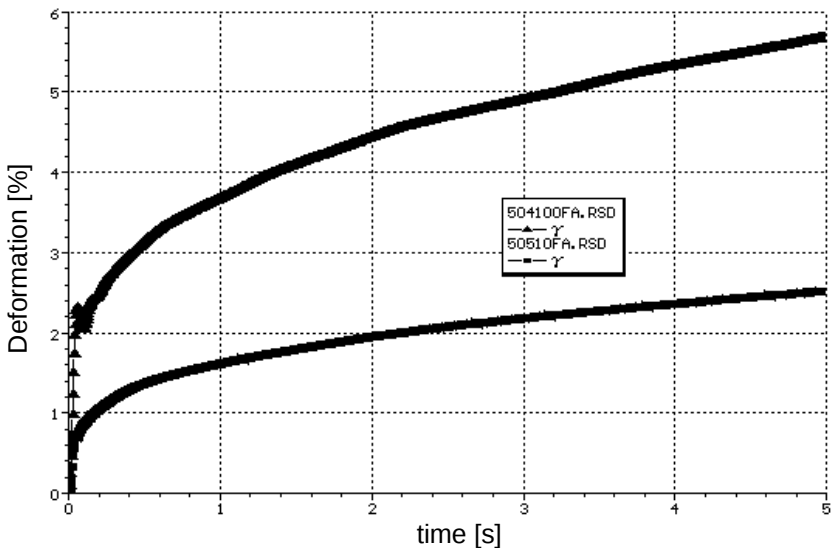


Fig. 173 Yield values of the printing inks explored in the more detail

Fig. 173: The creep curves of Fig.172 were re-plotted with the expanded initial phase of 5 sec to mark the yield values of the two inks more clearly. The are in fact much lower than one might have assumed looking at Fig.172.

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Rheology

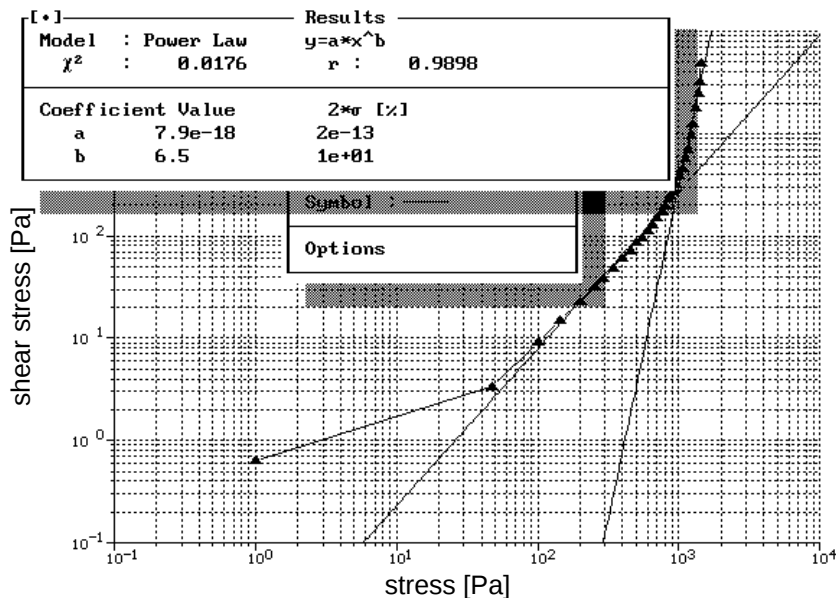


Fig.174 Yield value determination in a graph stress versus deformation by means of the intersect of the tangents

An alternative method of yield value determination is to plot the deformation versus shear stress using a double logarithmic scaling to cover a wide shear stress range. As long as the ink sample placed in the gap between the parallel-plates is still a solid, it is only elastically deformed by shear stresses being lower than the yield stress. The resulting deformation curve slopes upwards at a low angle characterizing the Young's modulus of the solid ink. When the yield stress is surpassed, the deformation curve changes its slope quite clearly. Regression calculation on the two segments of this deformation curve will provide tangents on those segments which intersect at the yield stress value.

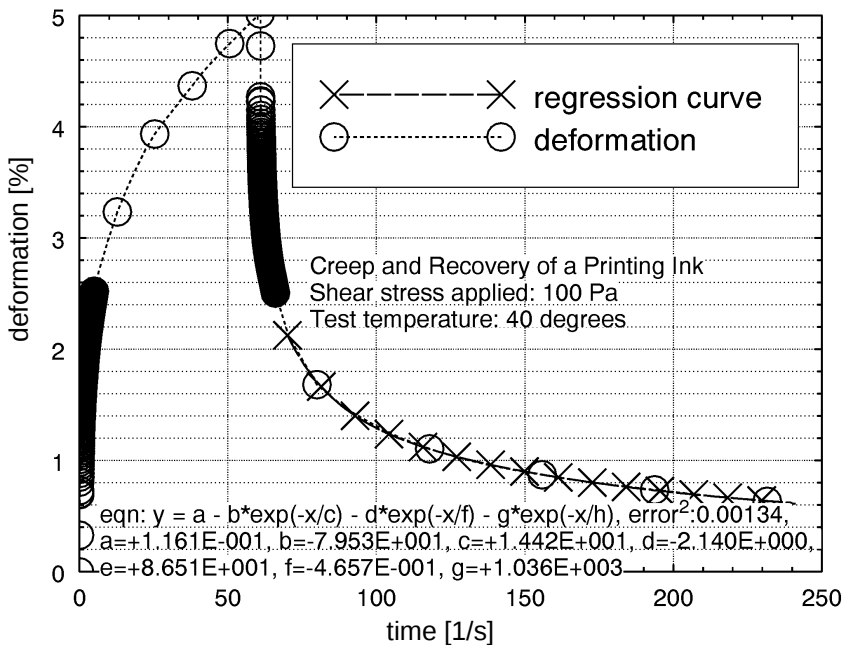


Fig. 175 Curve-fitting with a regression calculation on the recovery curve segment to define the coefficients for regressin equation

Fig. 175: A 3 minute recovery phase (60 to 240 seconds) is not sufficient for the elastic response of the strained ink to reach the recovery/retardation equilibrium. A curve-fit on the recovery curve with a suitable regression equation can provide the retardation time spectrum of this ink with 3 retardation time values:

$$\lambda_1 = c = 14.42$$

$$\lambda_2 = e = 86.51$$

$$\lambda_3 = g = 1036$$

This regression equation can be used to extrapolate beyond the 3 minutes of the actual recovery to mark the level of full recovery for an “infinite” recovery time. This value “a” derived from this extrapolation indicates that part of the initial deformation is maintained. It marks the viscous part in the visco-elastic response of the ink sample. Within 3 minutes of retardation time, the deformation has dropped to about 10 % of the maximum deformation at the end of the creep phase. At this moment one might classify the sample as 90% elastic and 10 % viscous.

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Please note: to look more closely at the deformation data in the very early phase of creep and recovery, the software stores 10-times more data than in the following phase: black curve segments.

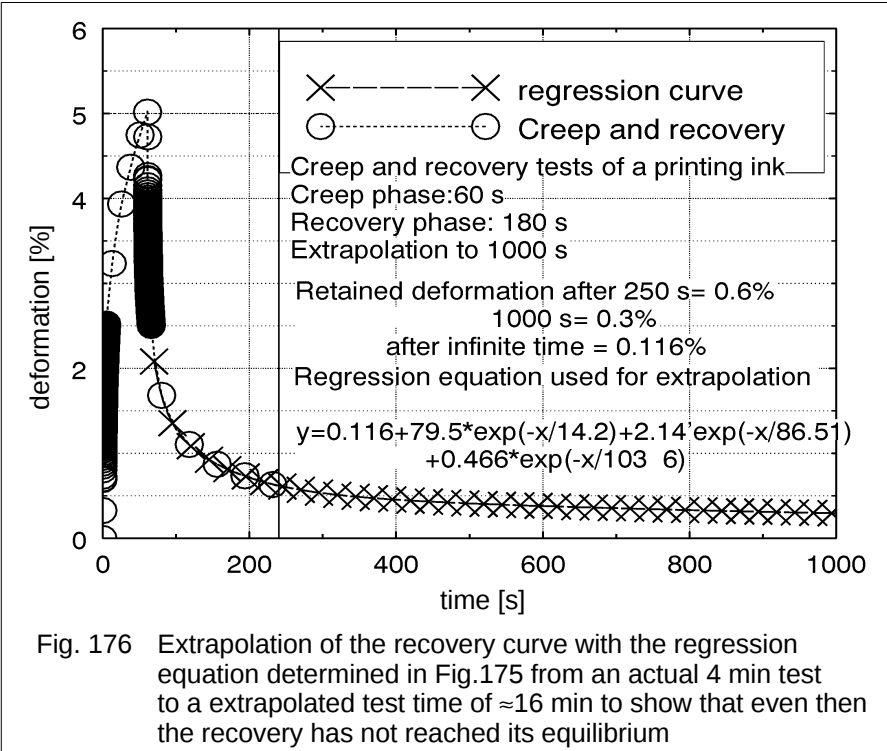


Fig. 176 indicates the effect of an extrapolated recovery phase on the ratio of elastic to viscous response during a prolonged retardation. After a 1000 sec (≈ 15 min) retardation time, the retained deformation is 0.2% which equals 4% of the initial creep deformation. At an infinite retardation time $x = t = \infty$, all the e-function of the regression equation becomes zero. The above equation then becomes $y = a = 0.116$ and this represents the retained deformation or the viscous component of the visco-elastic response of this ink within the framework of the chosen test conditions. At the infinite retardation time the ratio of the elastic to the viscous response becomes 98% to 2%. This should be kept in mind when the visco-elastic behavior is defined just by viscosity data or by short-term tests which do not allow the elastic component to become fully apparent.

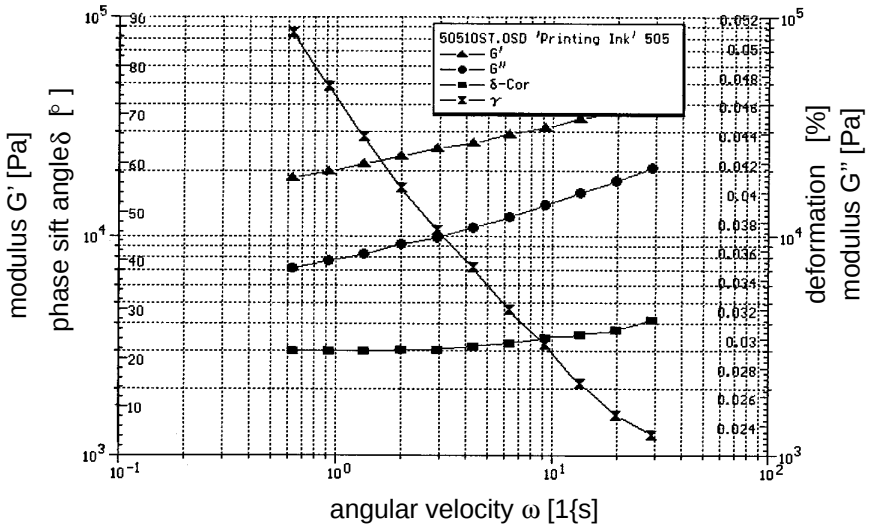


Fig. 177 Dynamic testing of a printing ink

Fig. 177 describes a printing ink by means of a dynamic test with respect to its loss modulus G'' – elastic response – and its storage modulus G' – viscous response as the function of the frequency. Added are also the curves of deformation γ and of the phase shift angle δ_{cor} , having been corrected for the influence of the rotor inertia. The ratio of elastic to viscous response changes with frequency ω . The chosen amplitude of $\tau = 10$ Pa had been determined in a preliminary test in order to guarantee that the dynamic tests are maintained within the boundaries of linear visco-elasticity.